

DEVELOPMENT OF AN OIL-WATER
POLLUTION MONITORING SYSTEM

Bruce Douglas Tyler

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THESIS

DEVELOPMENT OF AN OIL-WATER
POLLUTION MONITORING SYSTEM

by

Bruce Douglas Tyler

June 1975

Thesis Advisor:

T. M. Houlihan

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DEVELOPMENT OF AN OIL-WATER
POLLUTION MONITORING SYSTEM

by

Bruce Douglas Tyler
Ensign, United States Navy
B.S.O.E., United States Naval Academy, 1974

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

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June 1975

ABSTRACT

The prototype of an automatic oil pollution monitor was built and tested. In the system developed, a Direct Difference method of Total Organic Carbon determination was utilized to ascertain oil concentrations. Using this monitor, it was possible to specify the concentration of any oil, independent of type, in a known water sample. In the final phases of the study, preliminary investigations on prototype improvements and oil concentration determinations in bilge water were initiated.

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TABLE OF ABBREVIATIONS

Abbreviation	Definition
1. TC	Total Carbon
2. IC	Inorganic Carbon
3. NDIR	Non-Dispersive Infrared
4. VOC	Volatile Organic Carbon
5. JP-5	Navy aviation gasoline
6. NDFO	Navy Distillate Fuel Oil
7. MDO	Marine Diesel Oil
8. NSFO	Navy Special Fuel Oil
9. MS-9250	Navy heavy lube oil
10. MS-2190-TEP	Navy light lube oil

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I. INTRODUCTION

Ships, in the course of normal operations, routinely pump bilge and ballast water overboard. A National Academy of Sciences study has found that this water contains one-third of all of the oil that pollutes the ocean in a year. For this reason, the discharging of these major pollutants is now controlled by Federal Regulations (40 CFR 110; 36 FR 22489), which state that this discharge cannot (1) violate water quality standards and (2) leave a sheen. In addition, a goal of zero pollutant discharge was made by the 1972 Federal Water Pollution Control Act. Presently, regulations state that a 15 ppm oil concentration is to be the maximum allowable for navigable waters and a 100 ppm concentration is to be the maximum allowed elsewhere.

Overboard discharge of bilge and ballast water is, however, a necessary and vital operation if a ship is to remain at sea for any extended period of time. Smookler and Hardin [Ref. 1] have found that U. S. Navy ships generate a total of 4,000,000 gallons of bilge water per day. The in-port generation rate varies from 3,000 gallon per day rate for a destroyer up to 80,000 gallons per day rate for an aircraft carrier. These rates triple when the ships are underway. For this reason extensive research has

been performed in the area of oil-water separators. There are currently several operable separators that have a realizable discharge level of 20 ppm oil. The problem of monitoring separator discharge to be able to continuously determine the concentration of oil in the water, however, has not yet been solved.

Presently, the official Navy monitoring technique is the CCl_4 -I.R. Spectrometer method. This method has been shown to be slightly inaccurate, very time consuming and is basically a laboratory procedure. Therefore a great deal of research has been made into other methods of oil concentration measurement. The primary measurement techniques currently under study feature gas and gas-liquid chromatography, U. V. light absorption, optical density, conductivity, turbidity, infrared absorption, and carbon concentration determinations. All of these methods have inherent problems which have not yet been solved.

The optimum monitoring system should meet the following specifications:

- a.) be reliable and rugged enough to be used in a shipboard environment.
- b.) have a response to a particle size of 50 microns.
- c.) operate in a temperature range of 40° - 120°F .
- d.) have a fast response time.
- e.) be independent of oil type.
- f.) have an accuracy of ± 0.5 ppm in a 0-50 ppm range.

- g.) have a digital readout in ppm.
- h.) have automatic ranging.
- i.) be self-calibrating and ranging.
- j.) be self-purging and cleaning.
- k.) have short warm up and stablization times.

After a preliminary review of oil-water monitoring techniques in 1973, this investigator decided to experiment with a carbon analyzer monitor because (1) it was relatively untested in this application and (2) several operators of the analyzer indicated that it might be useful in an oil-water monitor application.

During FY 74 preliminary research was performed at the Naval Ship Research and Development Center in Annapolis, Maryland. The results of this research, by Prestia [Ref. 2] and Tyler [Ref. 3] , showed that a carbon analyzer could be used in a monitor application.

It was, therefore, the purpose of this research to build and to test a prototype of an oil-water monitor, using a carbon analyzer system, that met the prestated optimum monitor specifications.

II. THEORY

The determination of small quantities of organic matter in an aqueous solution was previously based on the wet oxidation method. In 1962, however, Montgomery and Thom [Ref. 4] developed a highly sensitive and accurate method for determining organic carbon concentration in water. Using this method, the sample is evaporated until dry. It is then burned in O_2 with all vapors being measured in an infrared analyzer. This process takes one to three hours per determination.

A more rapid method was developed in 1963 by Van Hall et al. [Ref. 5]. This system of determining total carbon concentration involves the vaporizing and oxidizing of a sample in a combustion tube containing a catalyst. The resulting CO_2 is then swept through a condenser and into a nondispersive infrared (NDIR) analyzer, sensitized to CO_2 , which relays a signal to a strip-chart recorder. Van Hall found that this system produced a linear variation between the recorder peak height and the total carbon concentration.

Based on this technology, Beckman Instruments, Inc., built a "Total Organic Carbon Analyzer." This instrument is similar to Van Hall's except that it employs two combustion tubes, one at $150^{\circ}C$ and the other at $950^{\circ}C$. The low

temperature tube contains quartz chips wetted with 85% phosphoric acid as a catalyst. Therefore, it oxidizes only inorganic carbons and some volatile organic carbons. The high temperature tube oxidizes all carbonaceous material. The difference between the NDIR measurements of the two chambers' combustion products is the total organic carbon concentration. A further explanation of the operation of this instrument is found in Appendix A. The use of this instrument to determine the concentration of oil in bilge water, however, involves further theoretical considerations.

Oil is a complex compound that has a variety of forms depending on the type. It was assumed for this research that oil is of the form $(CH_2)_n$. A correction factor, based on the C/CH₂ ratio of 14/12, was multiplied by the carbon concentration reading to obtain oil concentration values.

The effluent derived from present separator systems contains organic carbons other than oil. Seawater alone contains approximately 1.2 ppm organic carbon, as shown by Fredericks [Ref. 6] and Duursma [Ref. 7]. A correction factor that encompasses these additional organics was determined through experimental analysis and subtracted from the value of carbon concentration to yield ultimate results.

Bilge water, on U. S. Navy ships, has been characterized by Smookler and Hardin [Ref. 1]. In their study it was

found that bilge water was made up of three layers; surface, water and sediment. The water layer had an oil concentration of 15 ppm, 50% of the time, in port. At sea, the oil concentration in the water layer was below the regulation value of 100 ppm. Since the surface layer of oil in the bilge was just a thin film, it was theoretically possible to pump bilge water overboard a majority of the time without having to put it through a separation process.

The properties of bilge water that were assumed for this research project are based on the Smookler results. The first assumption was that a filtering process had been used in the separator system to remove the organic sediment contribution, which could be as high as 21 mg/l. The second assumption was that the major sources of bilge water were evaporator dumps and low pressure drains, therefore, making the bilge water approximately $2/3$ fresh water and $1/3$ salt water. The third assumption was that the major oil contaminant varies depending on ship compartment designation. In the fireroom it would be fuel oil and in the engineroom it would be lube oil.

III. EXPERIMENTAL PROCEDURE

A. INSTRUMENT DESIGN AND CONSTRUCTION

The basic instrument design was based on the Beckman Model 915 Total Organic Carbon Analyzer. This laboratory instrument provided the best construction and TOC determination method for adaptation into an automatic, shipboard, oil-water pollution monitoring system.

In order to implement the instrument construction, it was necessary to have an automatic sampling system. Ionics sliding block valves (Fig. 3) were selected as the main parts of this sampling system.

These valves, shown schematically in Fig. 1, contain a sliding block rulon and a channeled casing. The rulon features precisely drilled passages to carry measured sample sizes. In Position #1, air flows continuously through the air channel and the sample flows through the sample channel. Control air pressure forces the rulon to the right, as shown in Position #2, carrying a measured sample into the air stream, which forces the sample into the combustion tube. Subsequently, control air pressure then returns the rulon back to Position #1.

The air pressure used to set rulon positions is controlled by the normally open, 4-way, automatic, solenoid valves, shown in Fig. 2. These solenoid valves allow control air into one side of the sampling valves at a time.

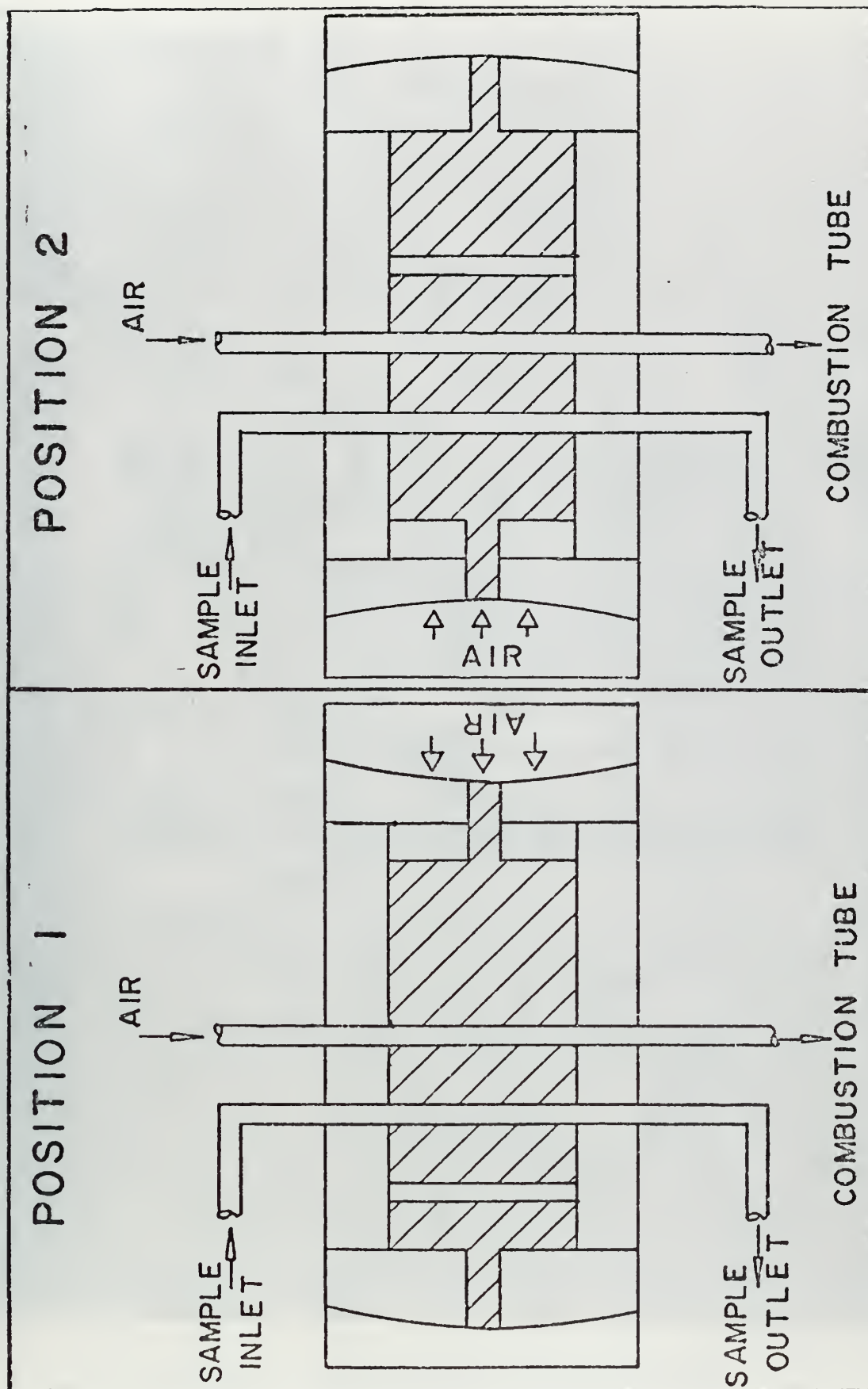


Figure 1. Sliding Block Valve Operation

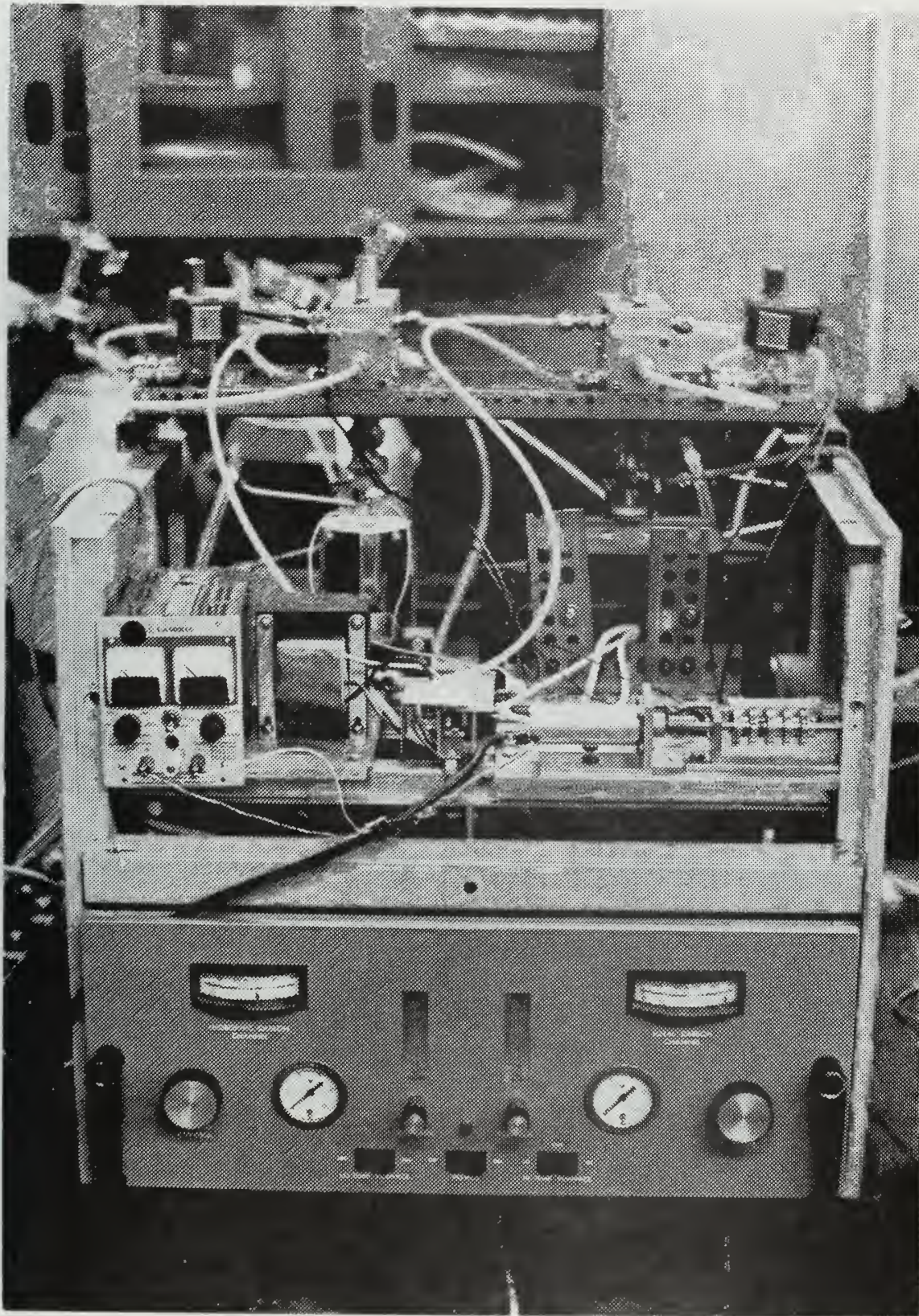


Figure 2. Sample-Inject/Furnace Module

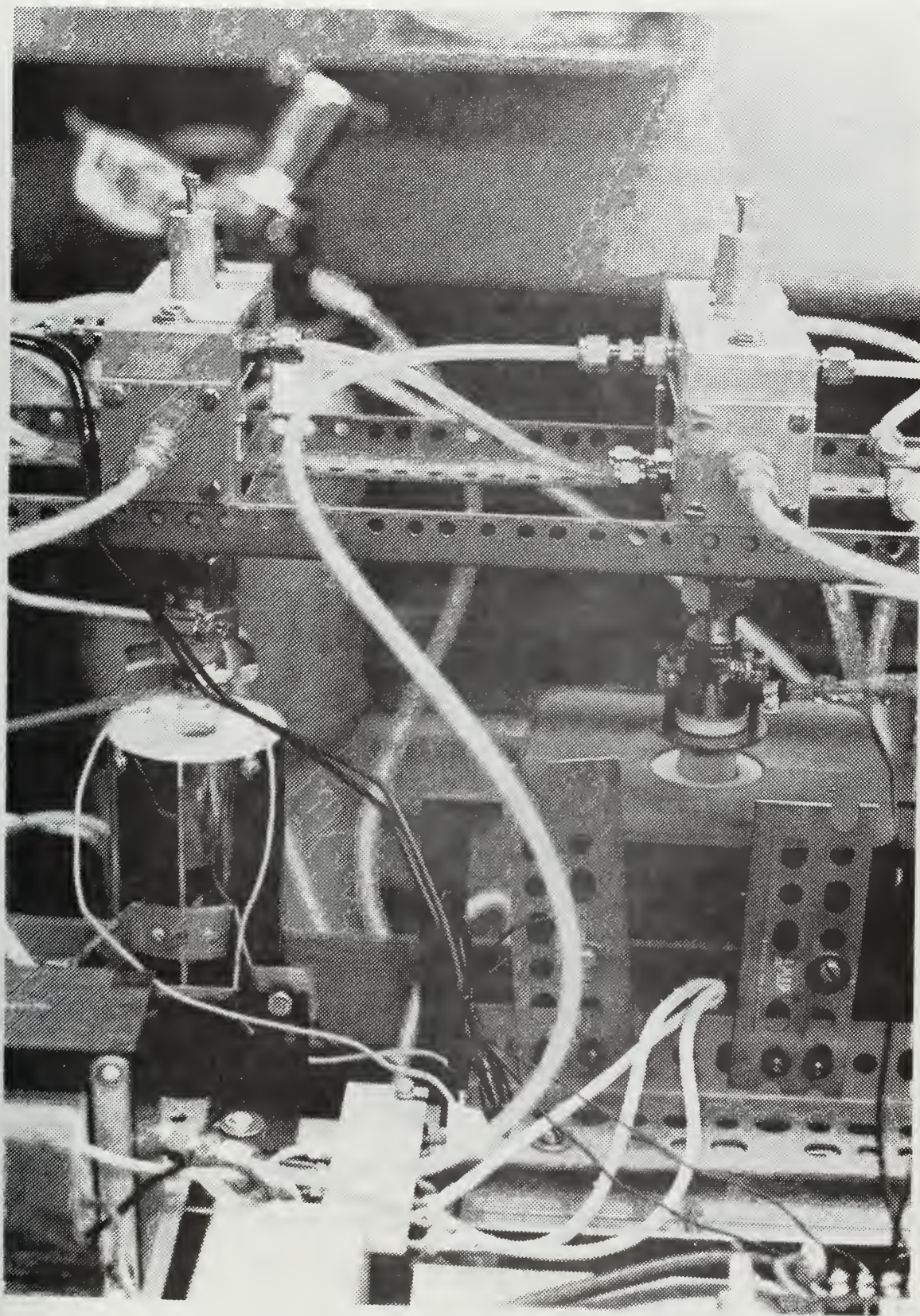


Figure 3. Sliding Block Valves and Combustion Tubes

In reverse operation, control air on one side of the valve is exhausted while the other side is filled.

To accomodate the sliding block valves and to enhance the operating performance of the system, the analyzer combustion tubes and ovens were changed from their original horizontal positions to vertical positions. The ovens were supported by frames that were attached to the walls of the Model 915. The combustion tubes were supported by L-brackets mounted on the floor of the Model 915, as seen in Fig. 4.

Connections between the combustion tubes and the sliding block valves were made with Swagelok fittings, as shown in Fig. 3. Injection tubes were run from the valve casing ports, through the Swagelok fittings and the sample inlet guides, and into the combustion tubes.

The flow system in the Beckman Model 915, as shown in Appendix A, was not adequate for automatic operation, so a new system had to be designed. The modified flow system, shown in Appendix B, allows the instrument to be run automatically by a timing control and allows for the use of a Volatile Organic Carbon (VOC) filter.

The first step in the modification was to remove the sample select valve and replace it with a series of normally open, universal flow, 3-way, automatic, solenoid valves. Next the tubing system was replaced, for the

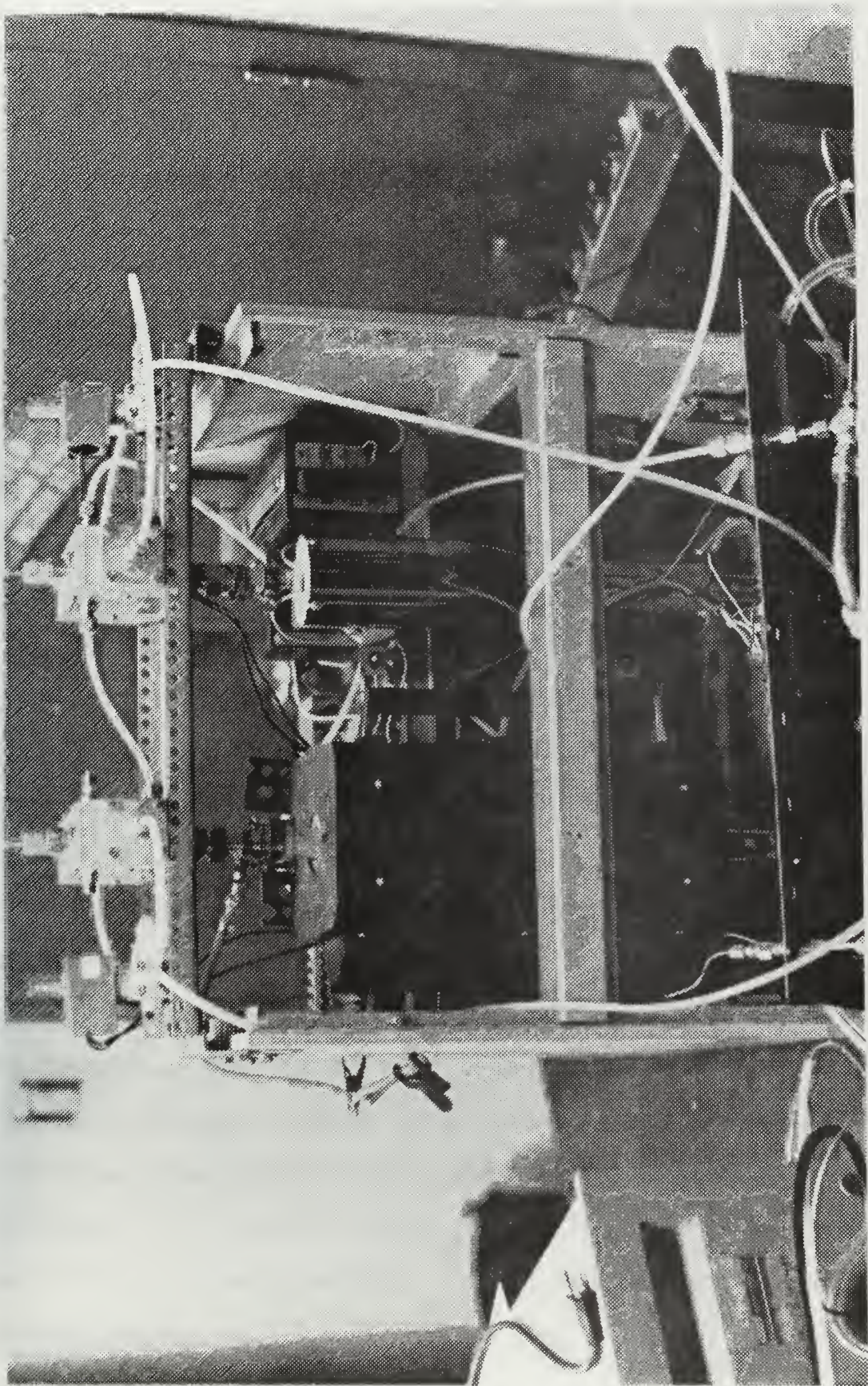


Figure 4. Rear View of the Combustion Tube Setup

most part, with 0.25" O.D. Poly-Flo tubing, with Swagelok fittings used at all interface connections.

When the combustion tubes were switched to the vertical position, a tubing attachment had to be made between the tube outlet and the condenser inlet (Fig. 8). Clean 0.25" I. D. Tygon tubing was used due to the possibility of high temperature contact.

Stainless steel condensers were used (instead of the older glass model condensers) to increase the ruggedness of the system. The condensers were angled at 45 degrees to allow for the free passage of steam and to reduce the condensation in the connection tube.

Solenoid valves #3 and #4 control the flow through the VOC filter. This directional filter requires that flow go in one direction to filter and go in the opposite direction to flush. The location of these valves is shown in Fig. 26.

Valve #5 controls the flow of air into the TC combustion tube. When an inorganic sample is injected, the valve is open so that the CO₂ and air from the IC combustion tube is brought up to the TC tube temperature before it enters the NDIR analyzer. This minimizes the baseline drift when switching channels for the different measurements. When a TC sample is injected, valve #5 is closed to the IC channel so that no excess inorganic carbon can cause a false measurement.

The operation of all the valves is controlled by the timing cams and micro-switches shown in Fig. 2. The timing cams were cut to give the sequence shown below in Table I. The timing motor was controlled by a variable voltage source which was set for a 5-minute cycle. The location of the numbered valves are shown in Fig. 26.

Valve Time	#1	#2	#3	#4	#5
0.0 min	1	0	0	0	1
2.5 min	0	1	0	0	0
2.6 min	0	1	1	1	0
2.7 min	0	1	0	0	0
5.0 min	1	0	0	0	1

1- Energized
0- Off

Timing Switch Chart for System Solenoid Valves

TABLE I

To prevent the samples from being contaminated, a Masterflex tubing pump (Fig. 5) was used to pump the sample from its beaker to the sliding block valve. Clean Tygon and Poly-Flo tubing was used along with a stainless steel Swagelok fittings to prevent contamination and corrosion.

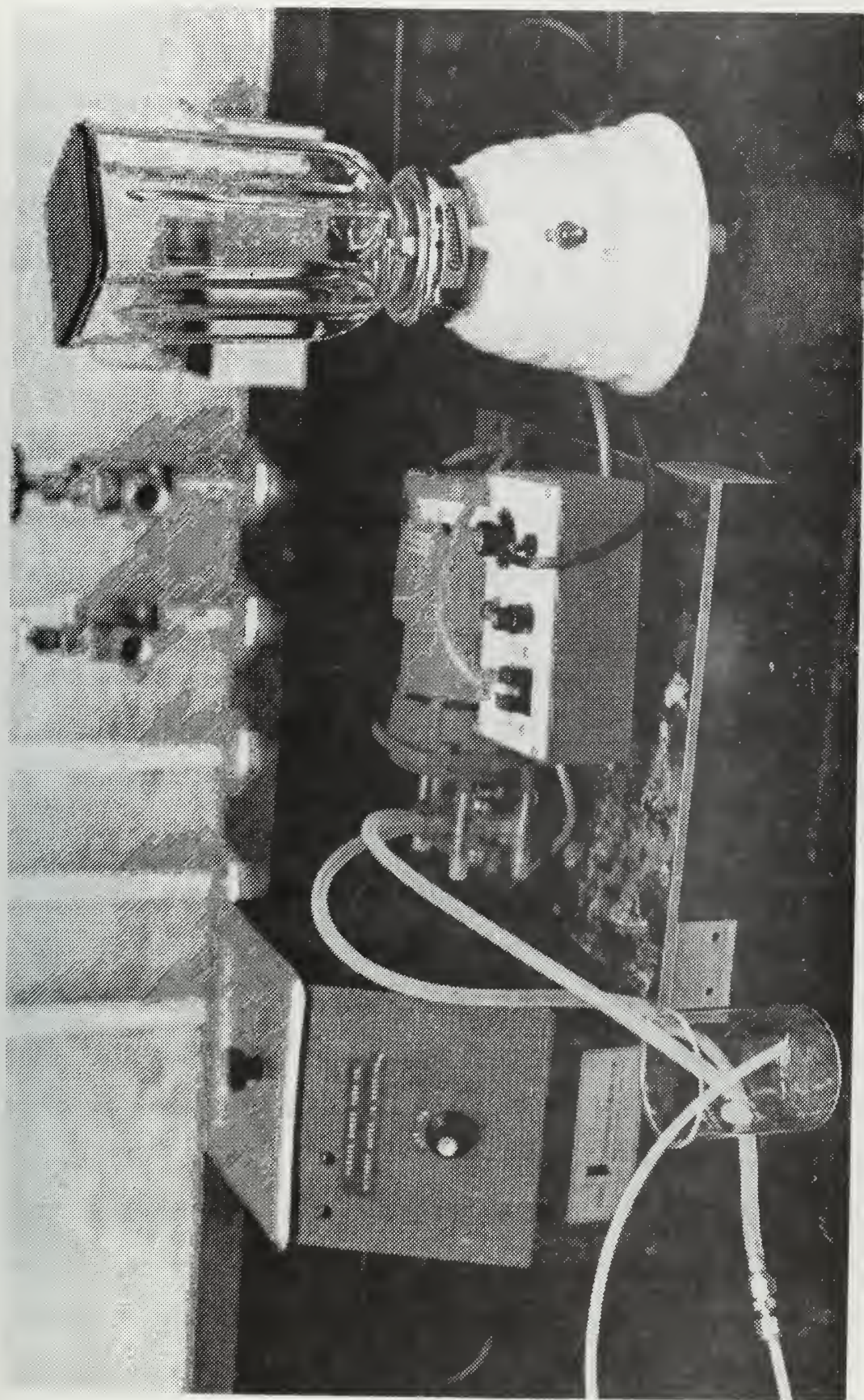


Figure 5. Sample Delivery System

The Model 215B and the Model 865 Non-Dispersive Infrared Analyzer, shown in Fig. 6, were tuned and adjusted for their maximum linear output. The output gain control was set by using an oscilloscope trace to obtain the peak performance level. The newer Model 865 was connected in series with the older Model 215B.

B. CALIBRATION

Prior to calibration, the system was tuned to achieve maximum performance. The instrument was ultimately operated at the settings listed in Appendix C. However, a test was first performed to find the optimum flow pressure and flow rate of the carrier gas. This test consisted of injecting a standard sample into the TC combustion tube, at various pressures and flow rates, and observing peak responses on the system strip-chart recorder (Fig. 6). It was found that a 4 psi pressure and a 250 cc/min flow rate gave a quick response, featuring a short peak with a uniform shape. This pressure and flow rate was maintained throughout the rest of the experiments.

The calibration of the system was done in accordance with the Beckman instruction manual [Ref. 8]. For the TC combustion tube, a 0.2125 gm sample of anhydrous potassium biphthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) was dissolved in 500 ml of distilled water, to yield a 200 ppm organic carbon solution. This solution was diluted with distilled water to give organic carbon stock solutions in the range of 0-50 ppm.

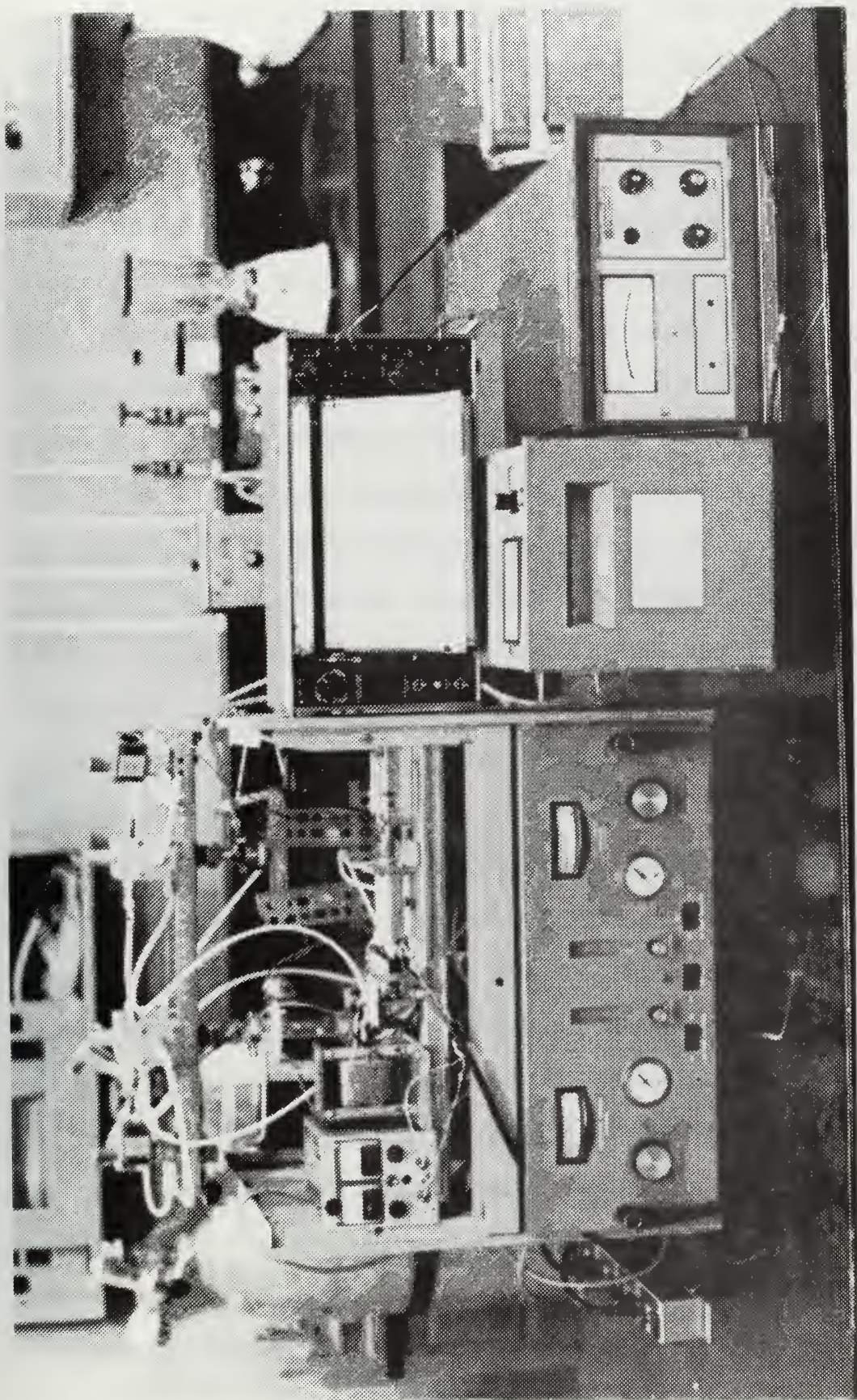


Figure 6. Total Monitoring System

The calibration process involved first injecting the distilled water to find its peak height and then injecting the distilled water-potassium biphthalate solution, with its known carbon concentration, to find its peak height. To find the relation between the peak height and the carbon concentration, the following equation was used;

$$(\text{Standard sample peak}) - (\text{Water peak}) = (\text{TOC peak})$$

Since there is no inorganic carbon in the sample, the TOC peak is directly related to the carbon concentration.

The inorganic combustion tube calibration was accomplished by dissolving 0.1101 gm of sodium carbonate (Na_2CO_3) and 0.0874 gm of sodium bicarbonate (NaHCO_3) in 500 ml of distilled water to yield a 50 ppm inorganic carbon concentration. This 50 ppm sample was diluted with distilled water to give inorganic stock solutions in the 0-50 ppm range.

The inorganic stock solutions were injected into both the inorganic carbon combustion tube and the total carbon combustion tube. Since the sample size for the two tubes was different, standardization curves using the inorganic stock solution were made for both channels. This provided a check on the TC calibration since a 50 ppm carbon sample of either stock solution should result in the same peak height. Since the distilled water used for the stock solution contains no inorganic carbon, the peak height recorded for the IC channel is the one related to the inorganic carbon concentration.

The weights of the compounds were determined by a difference measurement on a milligram balance. A plastic sample boat was first weighed and the desired compound was added until the exact amount was reached. The compound was then washed into a beaker with the 500 ml of distilled water.

C. OIL CONCENTRATION EXPERIMENT

This experiment was designed to prove the ability of the designed system to determine the concentration of oil in water. The oils used in this experiment ranged from a light, volatile oil to a heavy lube oil. The oils (JP-5, NDFO, MDO, MS-2190-TEP, and MS-9250) are U. S. Navy standards found onboard ships of the fleet.

Due to the sensitivity of the instrument, a careful standard procedure was used in this experiment. A clean blender was filled with about 200 ml of distilled water. This water was then blended for about 15 seconds and poured into a clean beaker. The suction tube, from the tubing pump, was placed in the distilled water. The water was then pumped through the injection circuit and the first 50 ml were drained off since it was acting as a cleanser for the system. Thereafter the discharge tube was placed in the beaker with the suction tube, thereby completing the circuit. This distilled water was run until a water peak baseline had been established.

The weight of the oil was established by first weighing a cleaned and wiped microliter syringe on the milligram balance. The syringe was "cleaned" by rinsing with acetone and distilled water, which prevented the addition of any measurable amounts of unwanted carbon into the system. The syringe was then filled with an amount of oil and weighed again. The difference was the weight of oil in milligrams. Care was taken in handling the syringe during weighing in order that no skin contact would be made with it. When the syringe was filled with oil only one suction stroke of the plunger was made in order to avoid any additional syringe contamination that pumping the plunger might involve.

The oil sample was then injected into the same blender that had the distilled water in it, along with 400 ml of distilled water. The oil concentration, in mg/l, was then known. For this experiment the concentration, in mg/l, was assumed to be equal to the concentration, in ppm. This solution was then blended for two minutes and the emulsion placed in the same beaker used for the distilled water. In this way an adequate control was maintained and any carbon contaminants could be accounted for.

The beaker was then placed in an ultrasonic cleaner which aided in keeping a uniform sample. The suction tube was placed in the beaker and the first 25 ml through the

injection circuit was treated as a rinse and allowed to drain off. Thereafter the discharge tube was placed in the same beaker with the suction tube, completing the injection circuit.

The system alternately injected samples into the inorganic and total carbon combustion tubes every two minutes, as controlled by the timing circuit. The output on the recorder was observed until several uniform peaks had been obtained.

After injecting several aliquots, the glassware was cleaned with detergent and water, then rinsed with distilled water and allowed to dry. The syringe was cleaned using the same method as before. Distilled water was pumped through the injection circuit to flush any oil that might coat the tubes.

During the injection process every oil-water emulsion was checked for a surface sheen or any other sign of incomplete mixing.

D. VOC FILTER TEST

A Porapak Q column filter, shown in Fig. 7, was obtained from Dohrman, Inc. This is a filter that separates CO_2 from organic compounds and is used by Dohrman in their Model DC-50 Total Organic Carbon Analyzer. The purpose of this filter is to trap any Volatile Organic Carbon (VOC) that might come out of the inorganic combustion tube along

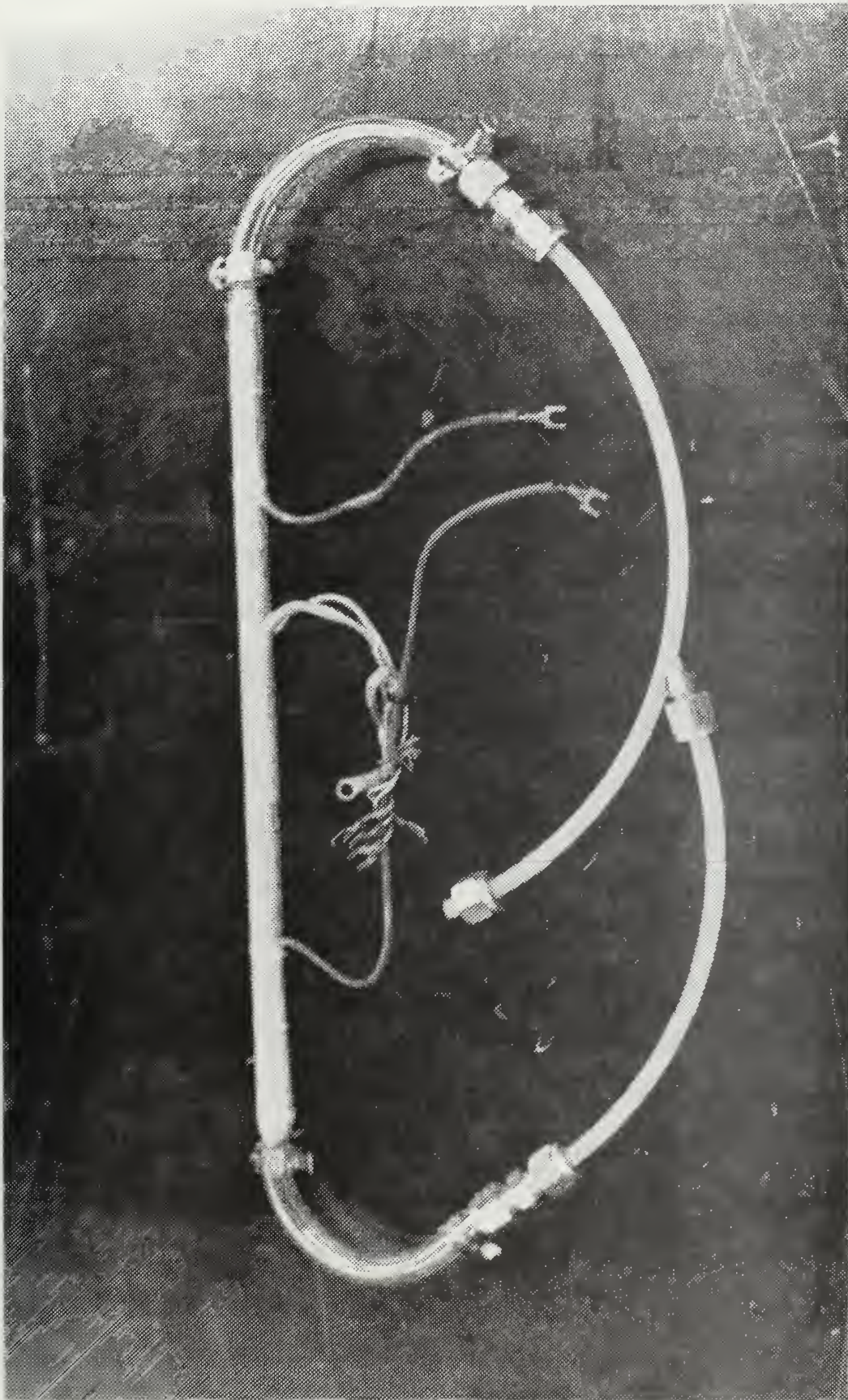


Figure 7. VOC Filter

with the CO₂ and steam. The filter is packed with an absorbant and traps the organic compounds at its entrance.

The VOC filter was originally installed for the purpose of increasing the accuracy of the instrument.

The filter was placed between valves #3 and #4, as shown in Fig. 26, to facilitate the filtering and purging operation needed for each inorganic carbon concentration. Swagelok fittings were used to connect the filter with the valves. The operation of the valves and the role of the filter is described in Appendix B.

E. BILGE WATER EXPERIMENT

To test the application of this system for shipboard use, a quantity of bilge water from a ship with an oil-water separator, was obtained. The bilge water was passed through a four-stage filter-coalescer and monitored by NSDRC, Annapolis. The "separated" bilge water's concentration was determined by using the I. R. Spectrometer-CCl₄ method, and found to contain less than 1 ppm.

The NSRDC bilge water was run through the system to determine the organic and inorganic carbon content. Since the "separated" bilge water had a concentration of less than 1 ppm, it was assumed to be representative of the carbon contribution by all bilge sources except for oil. For this reason the NSRDC bilge water was used as a base for oil concentration tests similar to those performed in Section C.

After the peak heights for the plain bilge water were found, NSRDC Oil Mixture #2 was added, using the same procedure found in Section C, to give varying concentrations of oil in bilge water. NSRDC Oil Mixture #2 consists of equal parts by volume of JP-5, DFM, NDF0, Hydraulic Oil, MS-9250, MS-2190-TEP, and NSF0.

In a beginning effort to establish a bilge water standard, sea water was run through the analyzer. The purpose of this test was to find the organic carbon contribution due to this component of bilge water.

F. ACID PURGE - INORGANIC TUBE COMPARISON

There are two currently used methods for determining TOC that are practical for pollution monitoring. The first, the one used by this system, is the Difference Combustion Method. This method finds both the total carbon and the inorganic carbon content. The difference between the two values yields TOC. The second is the Direct Acid Purge Method. This method acidifies the samples with 85% phosphoric acid, then purges them with nitrogen gas. The acid purge rids the sample of its inorganic carbon, leaving only TOC, which can be determined by injecting the purged sample in a high temperature combustion tube. An experiment was developed to test both techniques for possible use in a shipboard application.

A sample was first run through this system and the organic and inorganic peak heights recorded. The same sample was then acidified with one drop of 85% phosphoric acid per 10 ml of sample and then purged for six minutes with nitrogen gas, as per the procedure in the Amendum to the TWRI Manual. This purged sample was injected into both channels to determine the organic and inorganic peak heights. The results of the two methods were then compared.

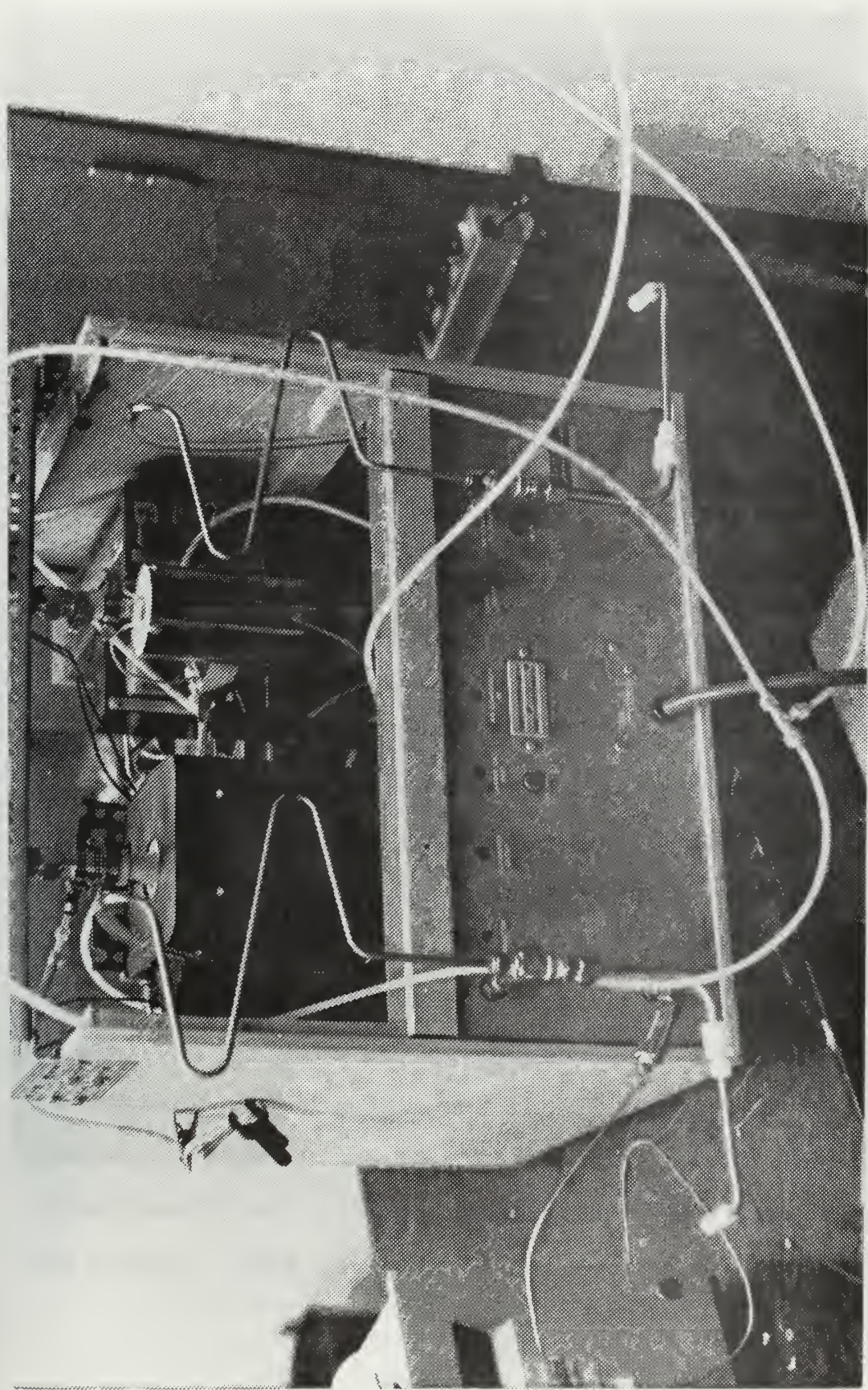


Figure 8. Rear View of Sample-Inject/Furnace Module

IV. RESULTS

A. PREFACE

The data taken from 1 May to 12 May was recorded using the Model 215B NDIR analyzer only. On 13 May the new Model 865 NDIR analyzer was placed in the flow, downstream from the Model 215B. The purpose of this was to compare the repeatability and operation of the two instruments. For this reason there are two peak heights recorded for every sample run after 13 May.

B. CALIBRATION

The results from the Total Carbon combustion tube calibration test are listed in Table II. The values are averages and standard deviations of the several aliquots that were run for each concentration level. The value of the standard deviation was primarily dependent upon monitor output peak height. There was no uniform variance. It was concluded that system repeatability was, therefore, primarily a function of the homogeneity of the solution.

The calibration data for the TC combustion tube is plotted in Figs. 9 and 10. The Model 215B calibration curves are linear but the intercepts do not pass through the origin. This is probably due to both the system

DATE	ANALYZER	MEASURED CONCENTRATION	TC PEAK	WATER PEAK	TOC PEAK
2 May	215B	50.0 \pm 0.1 ppm	84.2 \pm 2.7	3.4 \pm 0.1	80.8
"	"	25.0 \pm 0.1 ppm	45.4 \pm 1.7	"	43.0
"	"	12.5 \pm 0.1 ppm	25.9 \pm 1.0	"	22.5
"	"	6.3 \pm 0.1 ppm	15.8 \pm 0.8	"	12.4
"	"	3.1 \pm 0.1 ppm	9.4 \pm 0.7	"	6.0
3 May	"	50.0 \pm 0.1 ppm	82.0 \pm 0.6	3.3 \pm 0.3	78.7
"	"	40.0 \pm 0.1 ppm	69.2 \pm 2.6	"	65.9
15 May	"	40.0 \pm 0.1 ppm	61.9 \pm 0.7	2.5 \pm 0.7	59.4
"	"	20.0 \pm 0.1 ppm	33.9 \pm 1.9	"	31.4
"	"	10.0 \pm 0.1 ppm	18.9 \pm 1.2	"	16.4
"	"	5.0 \pm 0.1 ppm	11.5 \pm 0.8	"	9.0
"	"	2.5 \pm 0.1 ppm	6.8 \pm 0.6	"	4.3
"	865	40.0 \pm 0.1 ppm	75.2 \pm 1.9	4.1 \pm 0.6	71.1
"	"	20.0 \pm 0.1 ppm	41.0 \pm 1.8	"	36.9
"	"	10.0 \pm 0.1 ppm	23.4 \pm 1.3	"	19.3
"	"	5.0 \pm 0.1 ppm	14.6 \pm 0.7	"	10.5
"	"	2.5 \pm 0.1 ppm	9.3 \pm 0.5	"	5.2

Table II. TC Standard Solution Data

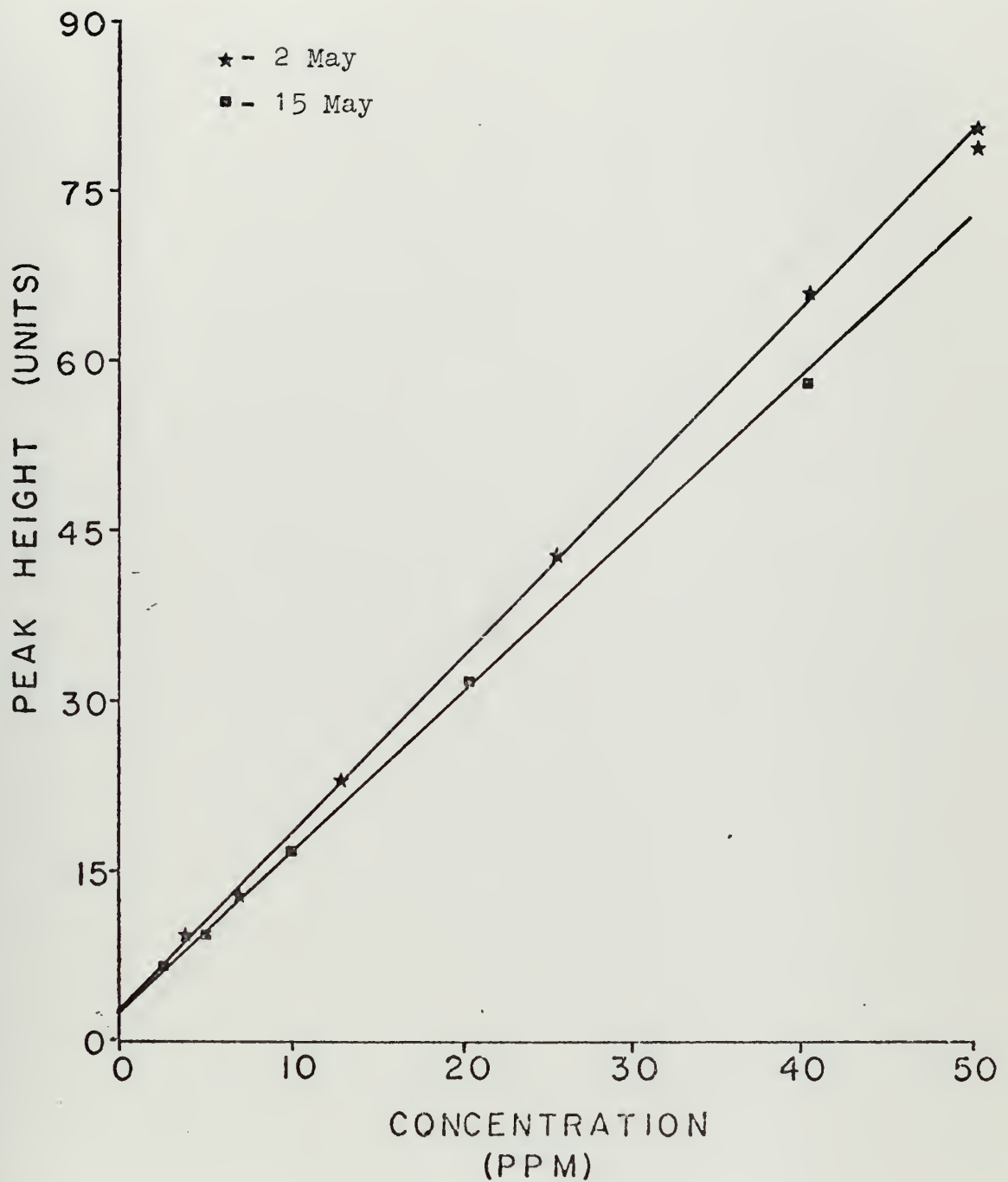


Figure 9. TC Standard Peak Height for Model 215B vs. Carbon Concentration

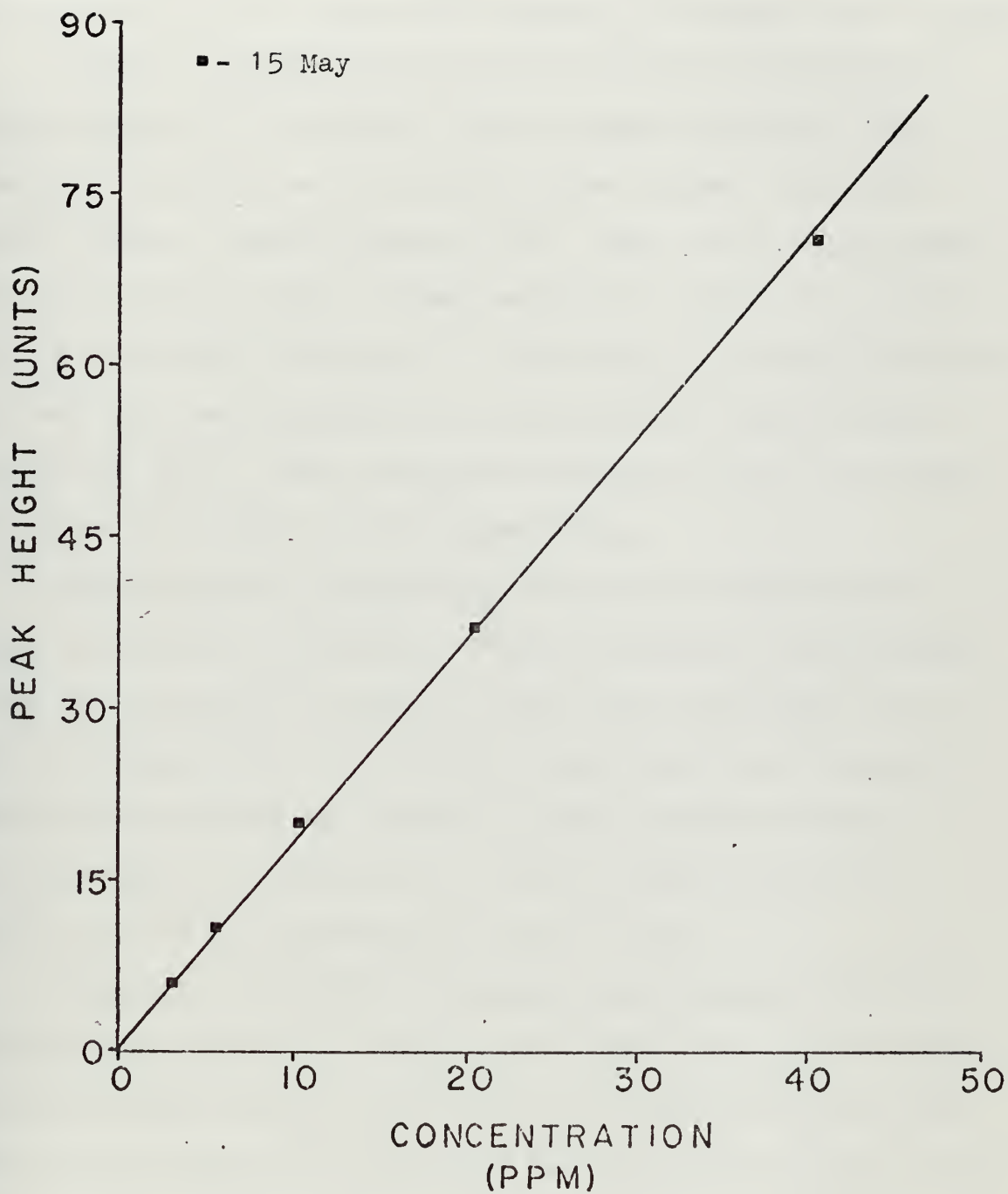


Figure 10. TC Standard Peak Height for Model 865 vs. Carbon Concentration

inaccuracies when measuring very low concentrations and inaccuracies in the initial determination of the concentration of the standard sample. The later Model 865 calibration curve is also linear and moreover intersects the origin.

Figure 11 compares the Model 215B and the Model 865 peak heights that resulted from the same solution. The Model 865 appears to be slightly more linear, over the entire range, than the Model 215B. This figure also shows the peak heights from the two analyzers differ by a factor of 1.17, for the TC channel. The reason for this difference is that the two analyzers are operating at two different values of gain. This variation continued to be a constant throughout the rest of the experiments.

The Inorganic Carbon standard solution calibration data is listed in Table III. The IC solution was injected into both combustion tubes to serve as a calibration for the IC channel and a calibration check for the TC channel. The reason for the difference in peak heights is that a 40 ul aliquot is injected into the TC tube and only a 20 ul aliquot is injected into the IC tube.

Figure 12 shows the IC channel calibration curves for both analyzers. It is readily seen that there is no decay in performance between the 14th of May and the 19th of May data even though oil injections had been made in the interim. The curves formed are again linear. However, the Model 865

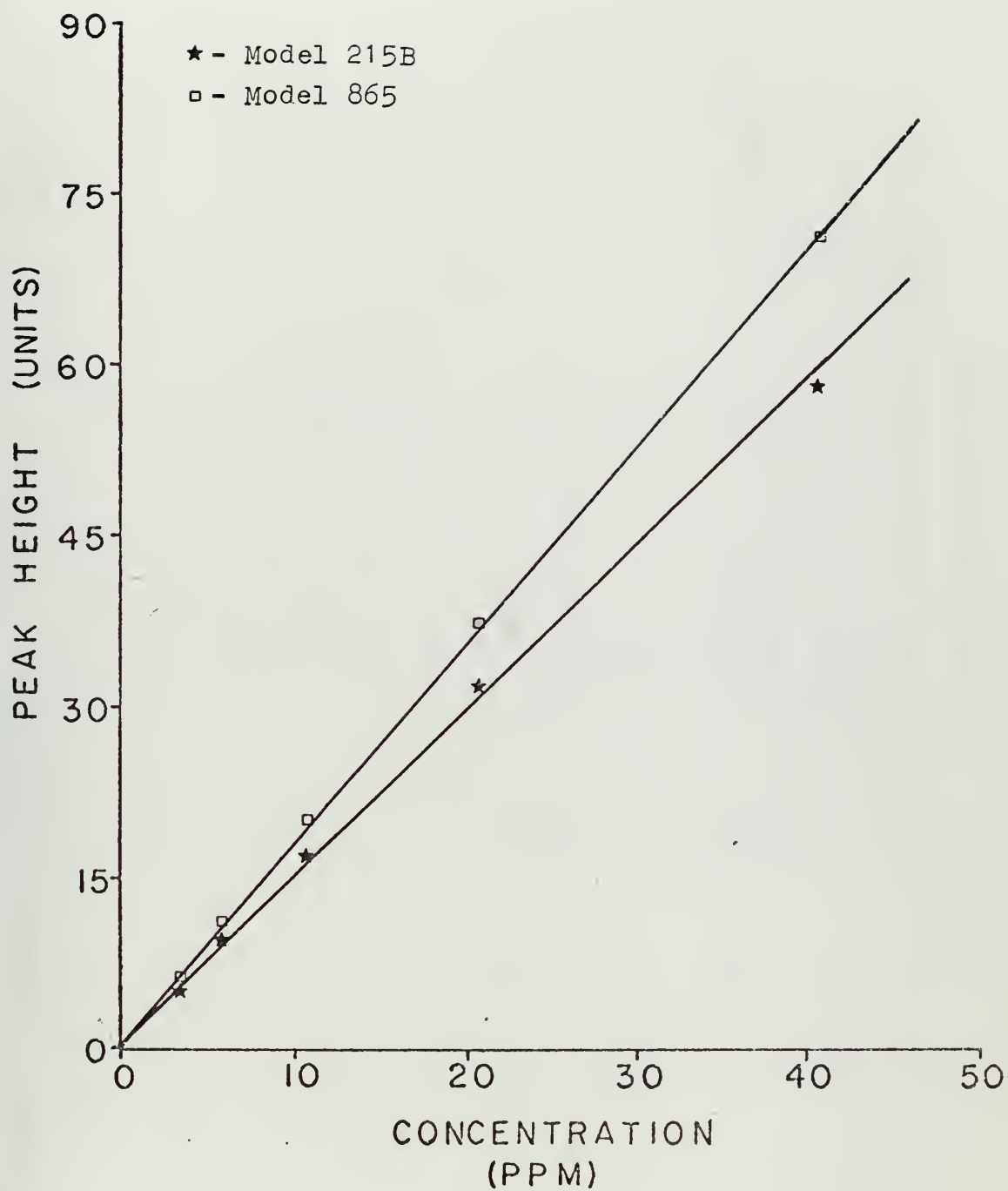


Figure 11. Comparison of Analyzer Output

DATE	ANALYZER	MEASURED CONCENTRATION	IC PEAK	TC PEAK	WATER PEAK
14 May	215B	40.0 \pm 0.3 ppm	15.4 \pm 0.8	65.2 \pm 1.3	3.4 \pm 0.3
"	"	20.0 \pm 0.3 ppm	8.3 \pm 0.3	34.6 \pm 0.8	"
"	"	10.0 \pm 0.3 ppm	3.5 \pm 0.0	20.2 \pm 0.9	"
"	"	5.0 \pm 0.3 ppm	1.5 \pm 0.1	10.8 \pm 0.3	"
"	"	2.5 \pm 0.3 ppm	0.7 \pm 0.1	6.2 \pm 0.3	"
"	865	40.0 \pm 0.3 ppm	21.6 \pm 1.1	77.2 \pm 1.6	5.7 \pm 0.3
"	"	20.0 \pm 0.3 ppm	12.3 \pm 0.7	43.3 \pm 1.0	"
"	"	10.0 \pm 0.3 ppm	6.0 \pm 0.3	25.4 \pm 1.0	"
"	"	5.0 \pm 0.3 ppm	3.2 \pm 0.2	14.8 \pm 0.4	"
"	"	2.5 \pm 0.3 ppm	2.0 \pm 0.1	10.1 \pm 0.5	"
20 May	215B	50.0 \pm 0.3 ppm	20.1 \pm 0.9	78.1 \pm 1.2	2.4 \pm 0.2
"	"	25.0 \pm 0.3 ppm	10.2 \pm 0.4	38.9 \pm 1.6	"
"	"	12.5 \pm 0.3 ppm	5.1 \pm 0.6	20.8 \pm 0.6	"
"	"	6.3 \pm 0.3 ppm	2.2 \pm 0.3	11.3 \pm 0.5	"
"	"	3.1 \pm 0.3 ppm	1.3 \pm 0.4	7.1 \pm 0.3	"
"	865	50.0 \pm 0.3 ppm	27.5 \pm 1.6	91.2 \pm 2.6	4.0 \pm 0.1
"	"	25.0 \pm 0.3 ppm	14.2 \pm 0.6	48.5 \pm 1.4	"
"	"	12.5 \pm 0.3 ppm	8.0 \pm 0.7	27.0 \pm 1.6	"
"	"	6.3 \pm 0.3 ppm	4.3 \pm 0.4	15.5 \pm 0.6	"
"	"	3.1 \pm 0.3 ppm	2.8 \pm 0.5	10.2 \pm 0.4	"

Table III. IC Standard Solution Data

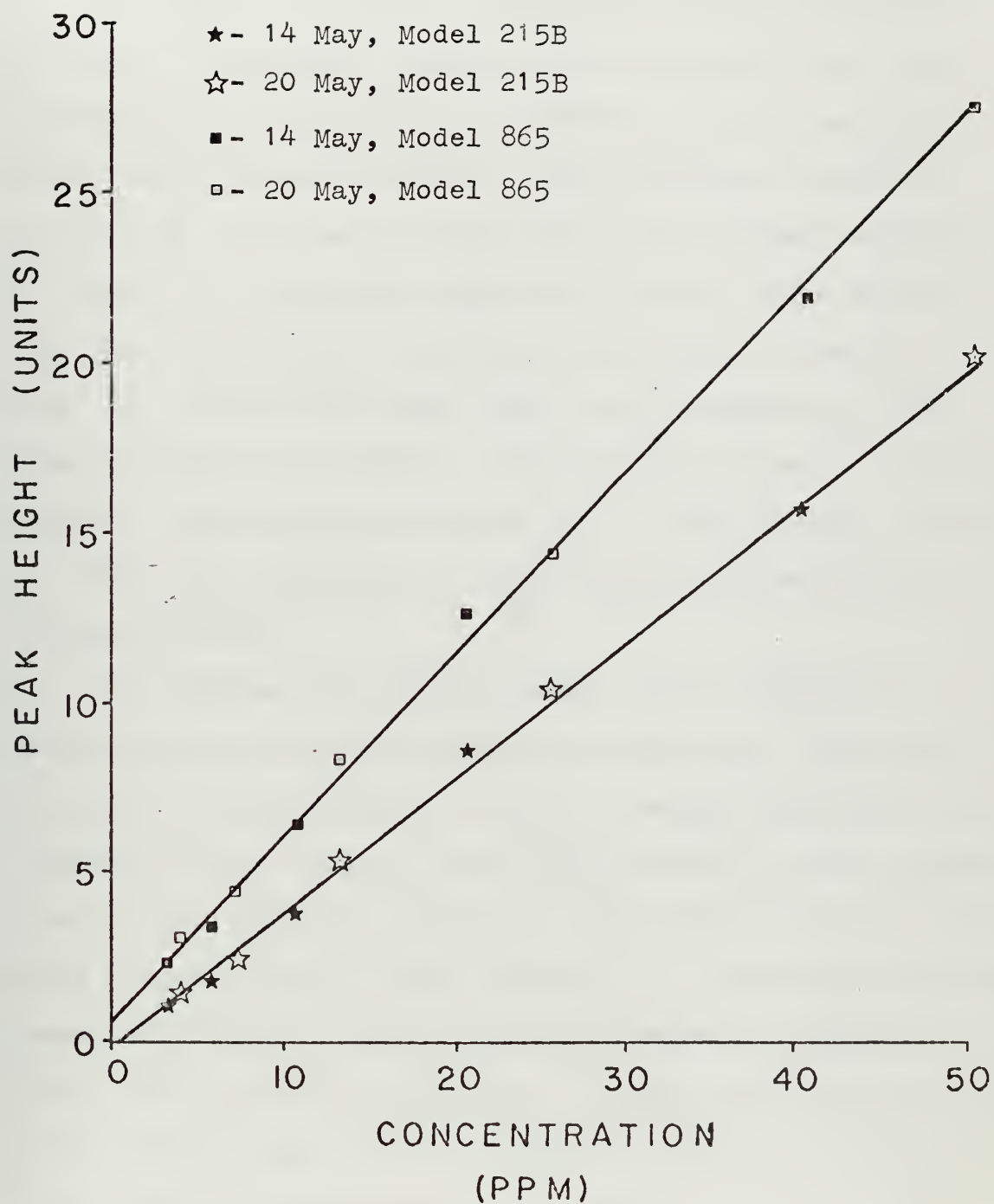


Figure 12. IC Standard Peak Heights vs. Carbon Concentration

line is 1.36 times greater than the Model 215B line. This variance is due to the increased accuracy of using a smaller peak height scale which gives better definition.

The results of the IC standard solution injections in the TC combustion tube are graphed in Fig. 13. The curves are linear with the exception of one data point which has a minor variation. The two curves are very similar to the ones plotted using a TC standard solution, in Fig. 11. The comparison of TC channel peak outputs for the two different standard solutions is found in Fig. 14. This curve shows that the TC channel has the same response to inorganic carbon that it does to organic carbon. For this reason Figs. 9, 10, and 12, will be used to find the concentration of an unknown, after finding its peak height.

The problem of catalyst decay and its effect on performance is best illustrated in Fig. 15. This graph of the Model 215B response to the TC standard solution, on different days, clearly shows the variance of the calibration curves with time and use. The 2 May and 15 May curves show a variation, at upper limits, of 4 ppm carbon for the same peak height. The variation between the 15 May and the 20 May curves is only minor. Since this instrument was under heavy useage (approximately 8 hours per day) there was a need to recalibrate once a week.

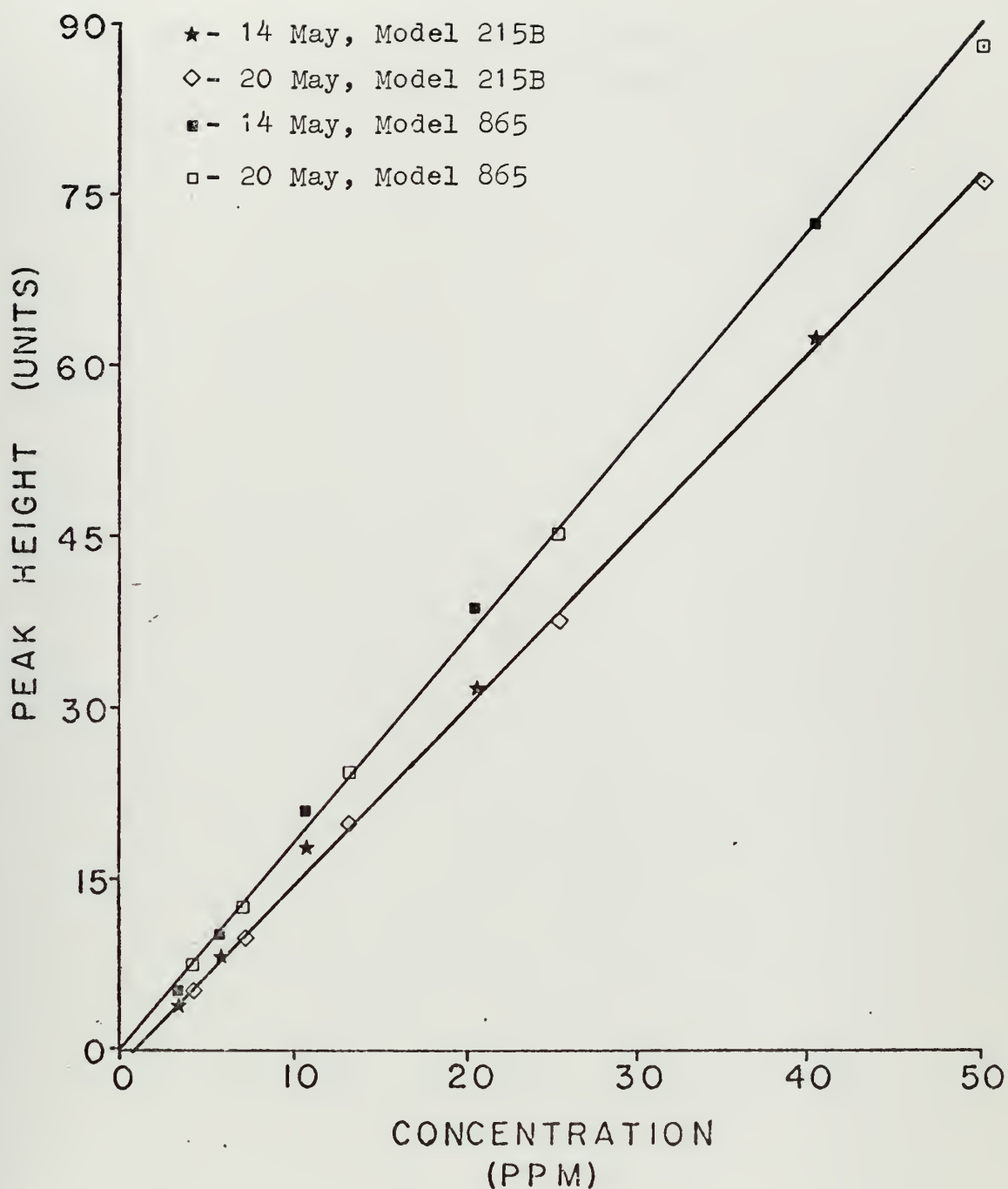


Figure 13. TC Channel Peak Heights using the IC Standard Solution vs. Carbon Concentration

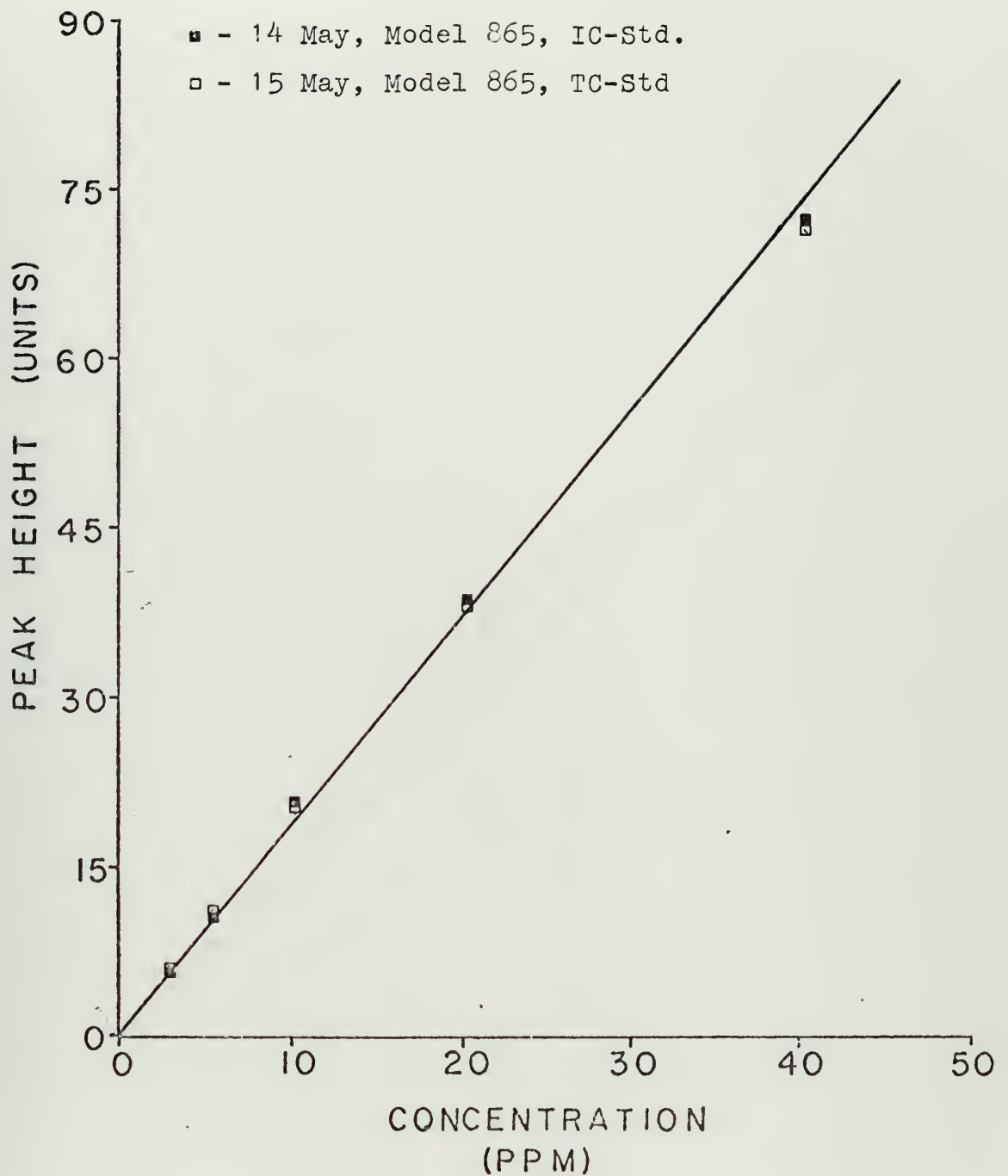


Figure 14. Comparison of TC Standard and IC Standard in the TC Channel

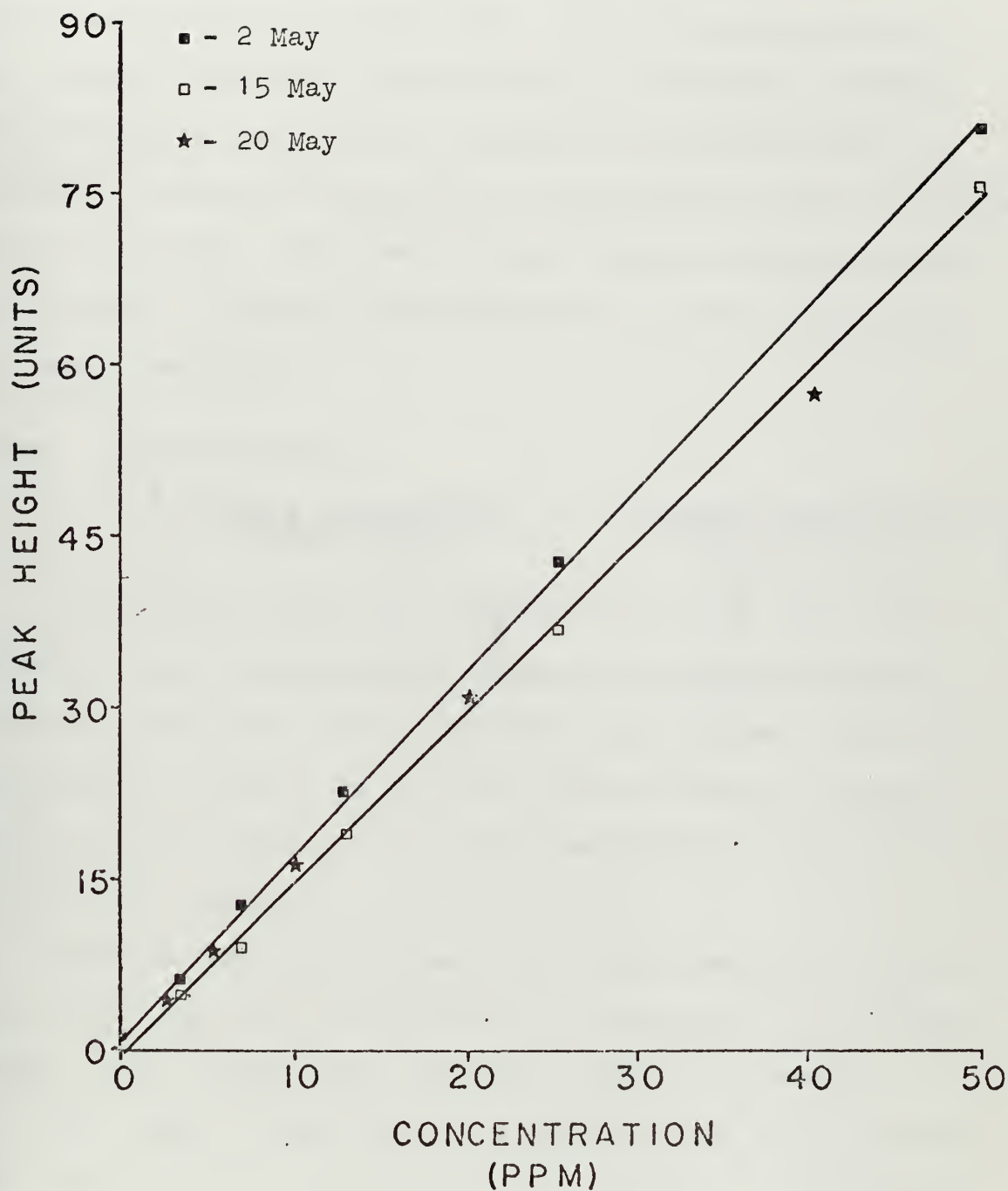


Figure 15. Effects of Time and Use on TC Calibration

C. OIL CONCENTRATION

The results of the oil concentration experiment are listed in Table IV. All the data in this section was taken using the Model 215B only. The TOC peak listing in the table is based on the fact that no inorganic carbon concentration was found in the water or the oil-water mixture, therefore making the TC measurement a TOC determination in reality. The error in the "Measured Concentration" section of the table, was determined by using the following error analysis:

Error = Concentration x

$$\left[\left(\frac{\text{weight uncertainty}}{\text{actual weight}} \right)^2 + \left(\frac{\text{volume uncertainty}}{\text{actual volume}} \right)^2 \right]^{\frac{1}{2}}$$

The TOC peak data are plotted along with the carbon standard curve concentration values, according to theory, are 1.17 times the carbon standard curve values. The oil data points all fall on or very close to the oil standard curve and the curve is most representative of the intersection of the data points.

Table V shows the comparison of the measured concentration and the concentration determined by using the oil standard curve. The average error, and therefore the accuracy, is 1.1 ppm. Most of that error is probably due to the method of sample preparation and delivery, instead of the system measurement.

DATE	OIL	MEASURED CONCENTRATION	TC PEAK	WATER PEAK	TOC PEAK
3 May	JP-5	46.5 \pm 0.6	71.0 \pm 2.9	7.3 \pm 0.3	63.7
5 May	"	19.3 \pm 0.5	28.3 \pm 0.6	2.7 \pm 0.5	25.6
"	"	25.0 \pm 0.5	40.6 \pm 1.6	"	37.9
"	"	41.6 \pm 0.6	73.6 \pm 2.5	13.3 \pm 0.5	60.3
"	"	28.5 \pm 0.5	54.2 \pm 2.6	"	40.9
6 May	MDO	25.0 \pm 0.5	37.5 \pm 1.7	4.7 \pm 0.5	32.8
"	"	39.8 \pm 0.5	60.1 \pm 4.5	2.8 \pm 0.1	57.3
"	"	4.2 \pm 0.5	8.6 \pm 0.4	3.2 \pm 0.2	5.4
"	"	32.8 \pm 0.5	49.6 \pm 1.8	2.5 \pm 0.3	47.1
7 May	NDF0	46.3 \pm 0.6	64.5 \pm 1.0	2.7 \pm 0.3	61.8
"	"	23.0 \pm 0.5	34.8 \pm 0.5	3.3 \pm 0.3	31.5
"	"	39.5 \pm 0.5	58.7 \pm 2.1	3.0 \pm 0.2	55.7
"	"	40.9 \pm 0.6	61.7 \pm 0.3	3.3 \pm 0.1	58.4
"	"	34.0 \pm 0.5	54.8 \pm 1.6	4.8 \pm 0.8	50.0
"	"	27.0 \pm 0.5	38.9 \pm 0.4	3.0 \pm 0.2	35.9
"	"	16.3 \pm 0.5	25.2 \pm 0.5	3.2 \pm 0.3	22.0

Table IV. Oil Concentration Experiment Data

DATE	OIL	MEASURED CONCENTRATION	TC PEAK	WATER PEAK	TOC PEAK
8 May	MDO	15.8 \pm 0.5	23.1 \pm 1.1	3.1 \pm 0.2	20.0
"	JP-5	5.6 \pm 0.5	12.8 \pm 0.4	2.9 \pm 0.2	9.9
"	NDF0	7.0 \pm 0.5	13.1 \pm 0.1	2.7 \pm 0.4	10.4
"	9250	20.5 \pm 0.5	48.9 \pm 0.9	32.6 \pm 0.5	16.3
"	9250	42.6 \pm 0.6	74.2 \pm 1.8	32.9 \pm 0.3	41.3
"	9250	20.8 \pm 0.5	51.2 \pm 0.2	34.5 \pm 1.0	16.7
21 May	NDF0	32.5 \pm 0.5	50.1 \pm 0.9	3.0 \pm 0.3	47.1
22 May	NDF0	9.5 \pm 0.5	18.3 \pm 0.3	3.8 \pm 0.2	14.5

Table IV. Continued

DATE	OIL	MEASURED CONCENTRATION	DETERMINED CONCENTRATION	ERROR
3 May	JP-5	46.5	46.0	0.5
5 May	"	19.3	18.0	1.3
"	"	25.0	26.8	1.8
"	"	41.6	43.5	1.9
"	"	28.5	29.1	0.6
6 May	MDO	25.0	23.5	1.5
"	"	39.8	41.2	1.4
"	"	4.2	3.0	1.2
"	"	32.8	33.5	0.7
7 May	NDFO	46.3	45.0	1.3
"	"	23.0	22.2	0.8
"	"	39.5	40.0	0.5
"	"	40.9	42.0	1.1
"	"	34.0	36.0	2.0
"	"	27.0	25.5	1.5
"	"	16.3	15.3	1.0
8 May	MDO	15.8	14.0	1.8
"	JP-5	5.6	6.2	0.6
"	NDFO	7.0	7.0	0.0
21 May	"	32.5	33.5	1.0
22 May	"	9.5	9.5	0.0

Table V. Oil Concentration Comparison Data

Due to the number of data points presented in Fig. 16, each oil was graphed separately to see if any type of oil had any distinct variations. Figures 17, 18 and 19 show that the oil standard curve is independent of oil type. Figure 17 shows the most variation because JP-5 is a very light oil making it very difficult to measure.

Figure 20 shows that the lube oil data, although linear, is distinctly lower than it should be. All the MS-9250 oil samples had a visible sheen which indicates that the samples were incompletely mixed. Further proof of this fact was found when a surface layer aliquot was injected and the peak height went off scale. The same problem of incomplete mixing also occurred in the MS-2190-TEP lube oil tests, therefore invalidating the data. This mixing problem in the heavier lube oils is due to their higher viscosity.

An important fact was found in running these oil concentration tests in that all that was needed to clean the system was distilled water. Although the system might be run continuously for close to an hour with an oil sample, this purging never took more than 10 seconds. Thus, consistently, the same peak heights were recorded for distilled water before every oil concentration run.

D. VOC FILTER TEST

The VOC column filter was installed on 12 May and the resulting output featured irregular and inaccurate peak

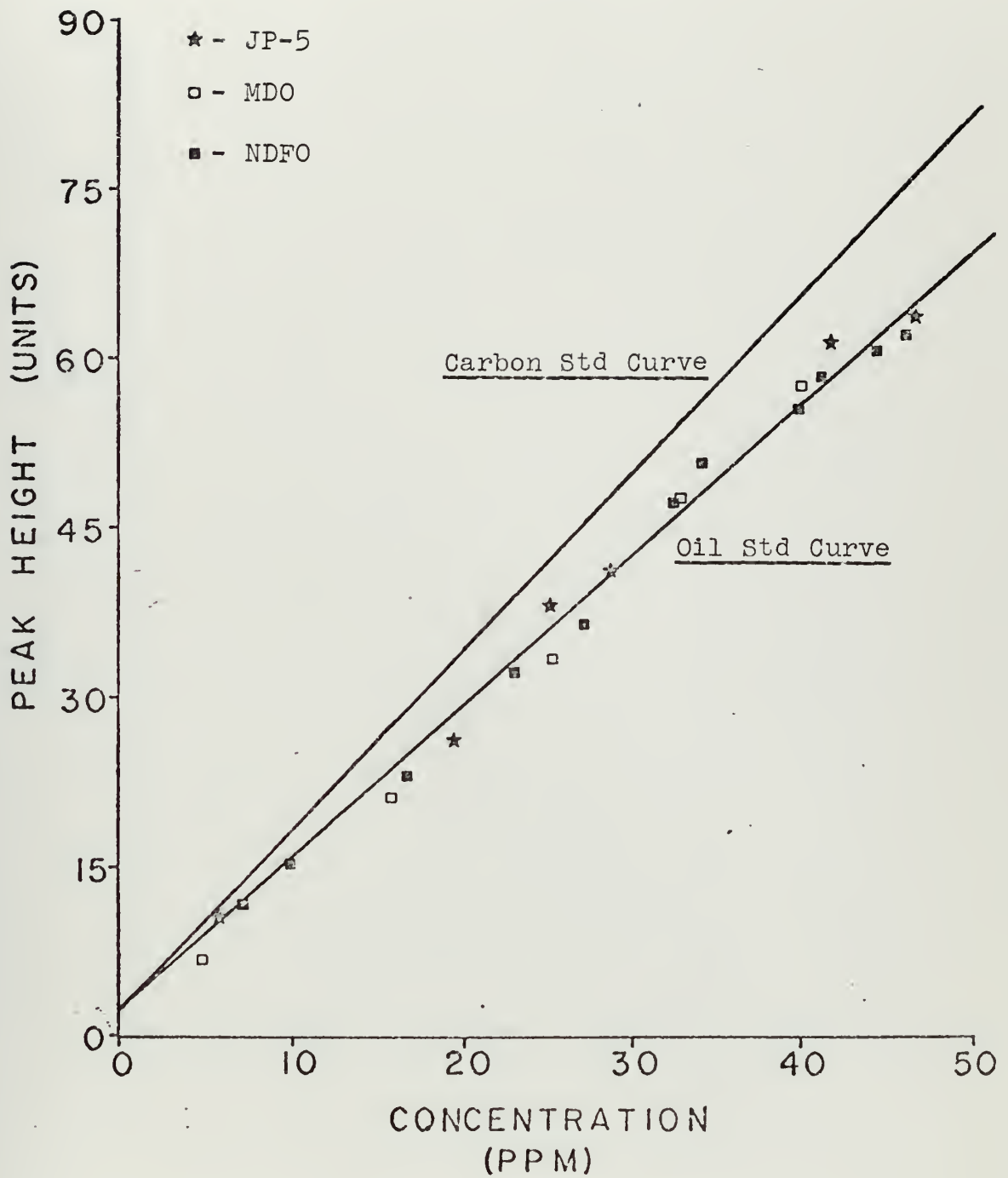


Figure 16. Oil Peak Heights with the Oil and Carbon Standards vs. Concentration

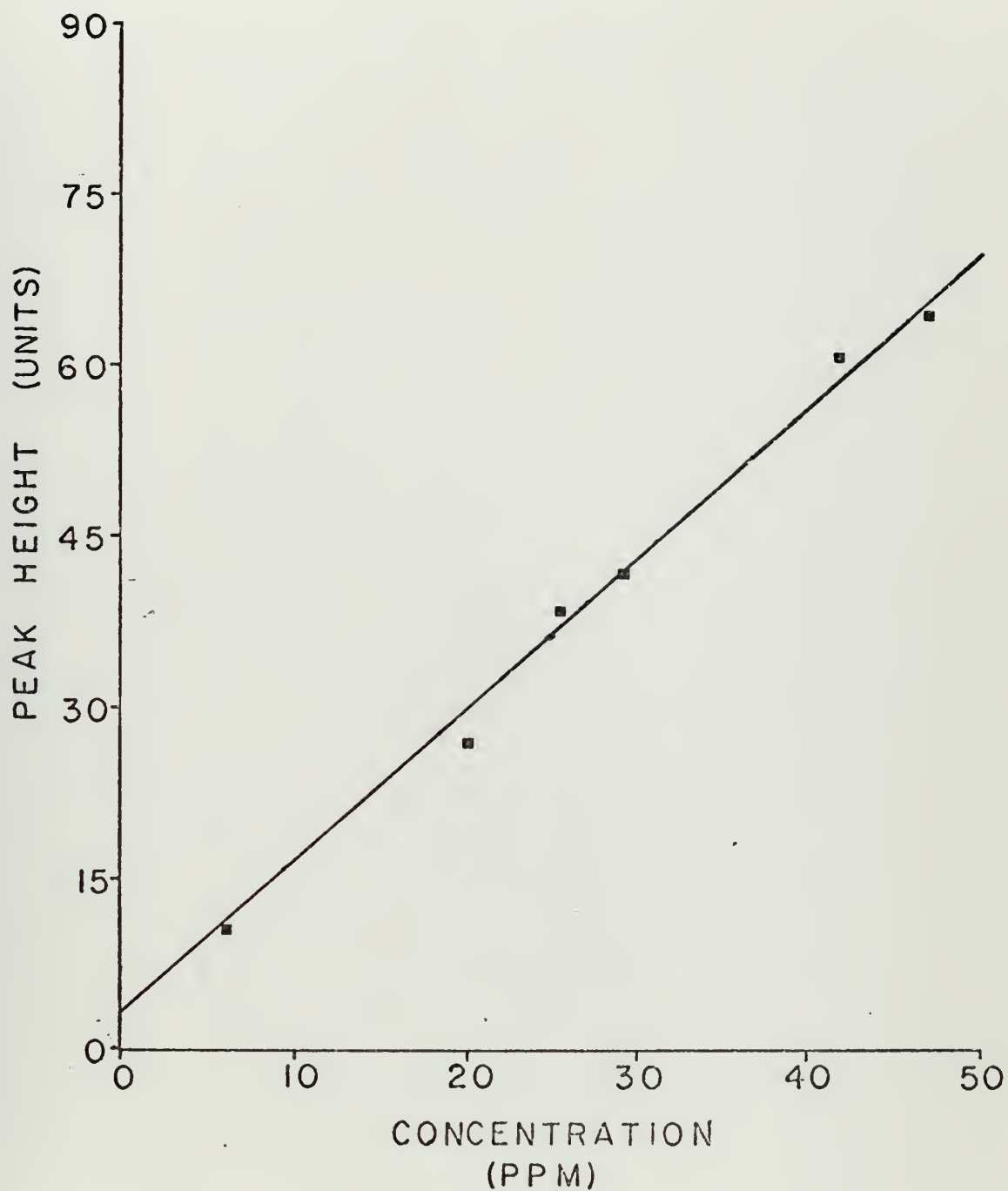


Figure 17. JP-5 Peak Heights with the Oil Standard Curve vs. Concentration

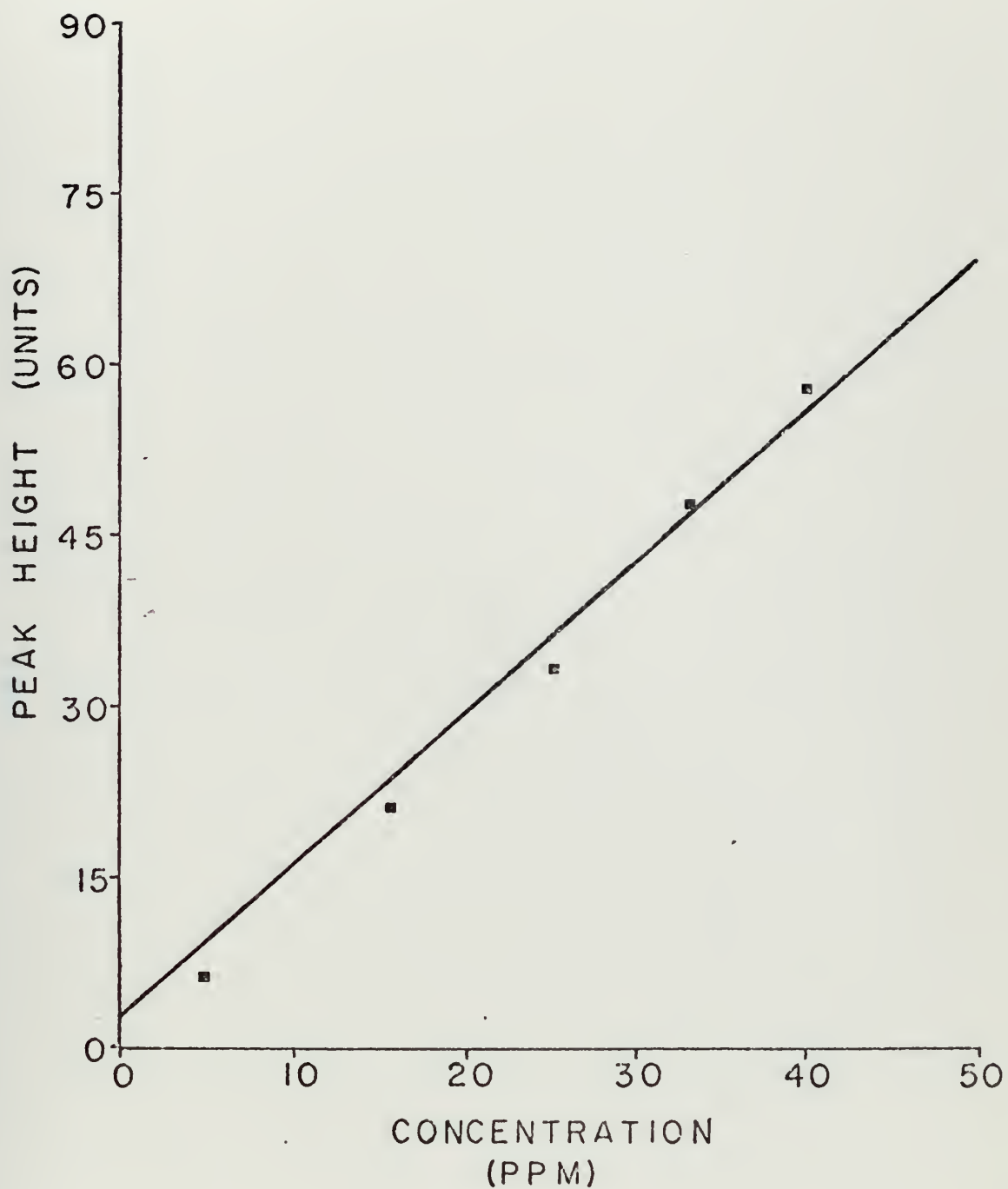


Figure 18. MDO Peak Heights with the Oil Standard Curve vs. Concentration

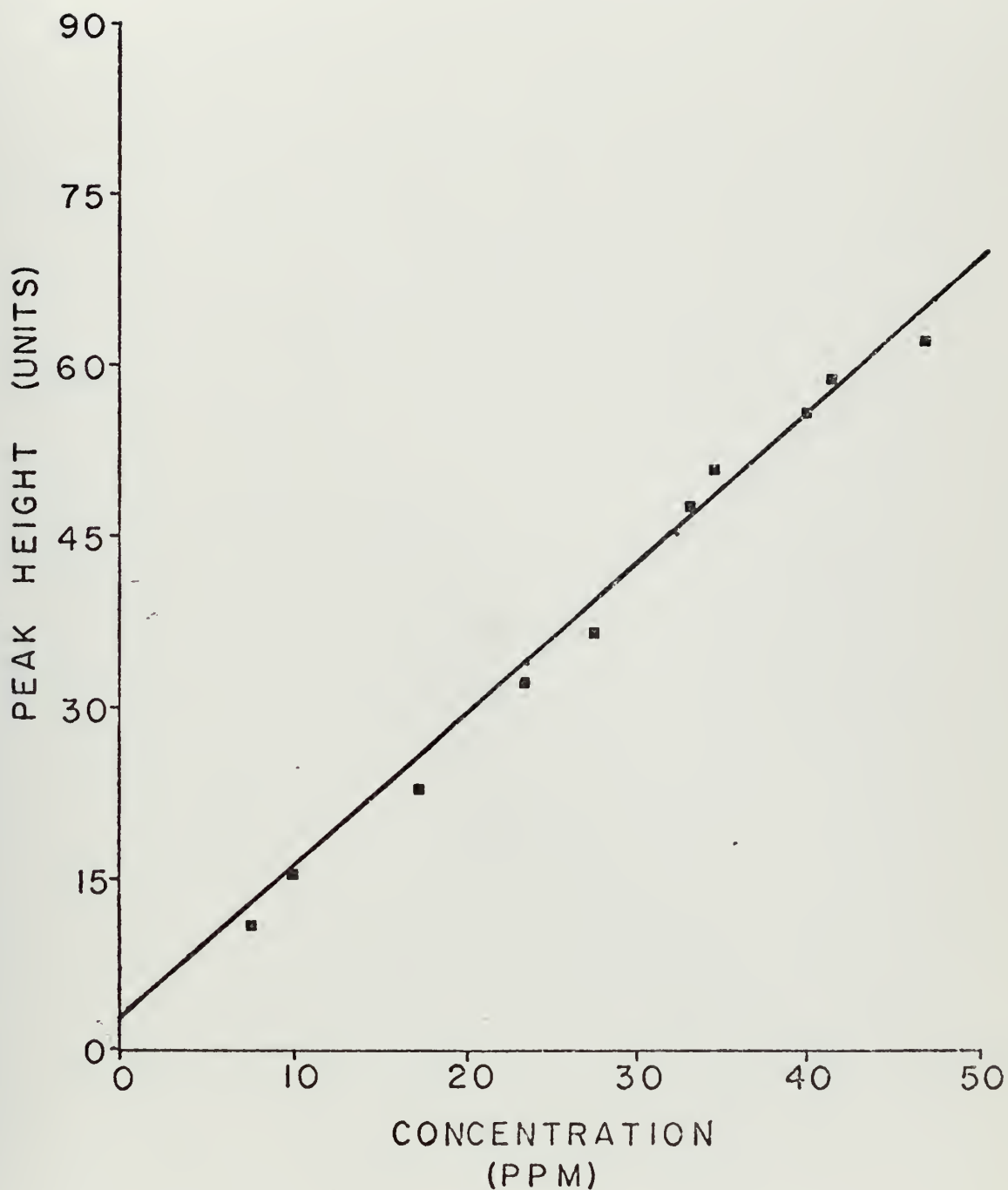


Figure 19. NDFO Peak Heights with the Oil Standard Curve vs. Concentration

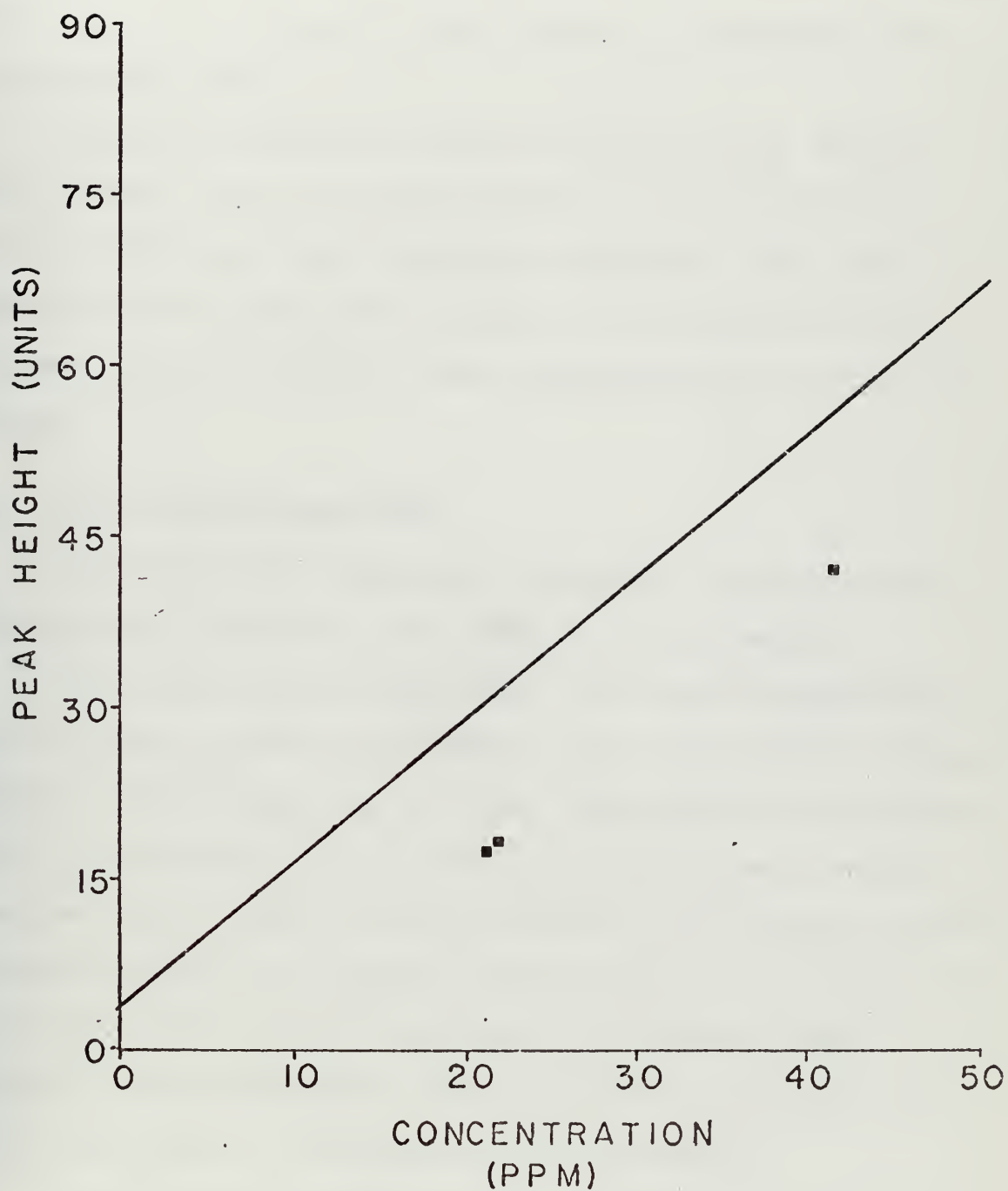


Figure 20. MS-9250 Peak Heights with the Oil Standard Curve vs. Concentration

heights. The peak heights that resulted are shown in Fig. 21. The filter was promptly removed but the double peaks persisted. This indicated a possible valve contamination, so valves #3 and #4 were removed. The system then returned to normal.

Since the purpose of the VOC filter was to improve the accuracy and the results showed an incompatibility, future testing of the filter was suspended. The part of the system that was used to support the operation of the filter, valves #3 and #4, were permanently left out of the system.

E. BILGE WATER EXPERIMENT

The preliminary tests on "separated" bilge water are summarized in Table VI. The results are threefold.

First the tests on the NSRDC bilge water showed that the inorganic carbon concentration was 6 ppm and the organic carbon concentration was 7.5 ppm. Since the oil concentration, as determined by the CCl_4 -I.R. Spectrometer method, was less than 1 ppm, it had no effect on the carbon content. The concentration of carbons, other than oil, is seen to be of a low level, therefore making it possible to have a standard compensating value that would be subtracted from the bilge water to determine oil concentration.

Since seawater makes up about one-third of the bilge water content, according to theory, its carbon concentration

DATE	ANALYZER	SAMPLE	MEASURED CONCENTRATION	TC PEAK	WATER PEAK	IC PEAK	TOC PEAK
15 May	215B	B.W.	-	21.6 ± 0.8	-	2.0 ± 0.1	-
23 May	"	"	-	20.9 ± 0.6	-	1.7 ± 0.2	-
25 May	"	"	-	21.5 ± 0.5	-	2.0 ± 0.1	-
15 May	865	"	-	25.5 ± 0.4	-	4.0 ± 0.0	-
23 May	"	"	-	25.1 ± 0.4	-	3.6 ± 0.4	-
25 May	"	"	-	25.9 ± 0.5	-	3.9 ± 0.1	-
"	215B	S.W.	-	43.3 ± 1.5	-	6.7 ± 0.4	-
"	865	"	-	49.4 ± 1.3	-	10.1 ± 0.6	-
15 May	215B	Oil #2	21.5 ppm	49.3 ± 1.0	20.7 ± 0.5	1.7 ± 0.2	28.6
"	865	"	"	58.0 ± 1.3	25.1 ± 0.4	2.6 ± 0.4	32.9
23 May	215B	"	33.3 ppm	62.2 ± 0.2	20.9 ± 0.6	1.7 ± 0.2	41.3
"	865	"	"	73.2 ± 0.2	25.1 ± 0.4	2.6 ± 0.4	48.1
"	215B	"	23.5 ppm	50.6 ± 0.5	20.9 ± 0.6	1.7 ± 0.2	29.7
"	865	"	"	58.4 ± 0.6	25.1 ± 0.4	2.6 ± 0.4	33.3
"	215B	"	14.3 ppm	39.1 ± 0.3	20.9 ± 0.6	1.7 ± 0.2	18.2
"	865	"	"	45.7 ± 0.4	25.1 ± 0.4	2.6 ± 0.4	20.6

Table VI. Bilge Water Experiment Data



Figure 21. Sample Peak Heights with VOC

was found. The inorganic concentration was 17.5 ppm and the organic value was 10.3 ppm. The organic value was high for ocean water but the seawater was taken from the surface in a bay which accounts for the high values. These results indicate that the seawater is probably less than one-third of the bilge water make-up.

The last test was an oil concentration experiment again using the NSRDC bilge water. Figure 22 shows the results plotted with the respective oil standard curves pertaining to each NDIR analyzer. All the data points are very close indicating that oil concentration in bilge water can be found if the organic and inorganic carbon content of the bilge water without oil is known. The reason that the data points are slightly but uniformly lower than the oil standard curve is that the curve is based on the calibration data from the previous week which has decayed slightly due to catalyst action. The results further show that the oil standard curve is independent of oil type, since NSRDC Oil Mixture #2, was used, making it suitable for bilge water determinations.

When testing the bilge water, it was found that two baseline levels were appearing, depending on which channel was being used. This result could have only been attributed to the #5 valve, which controls the IC channel flow. This valve was removed and the resulting baseline became level.

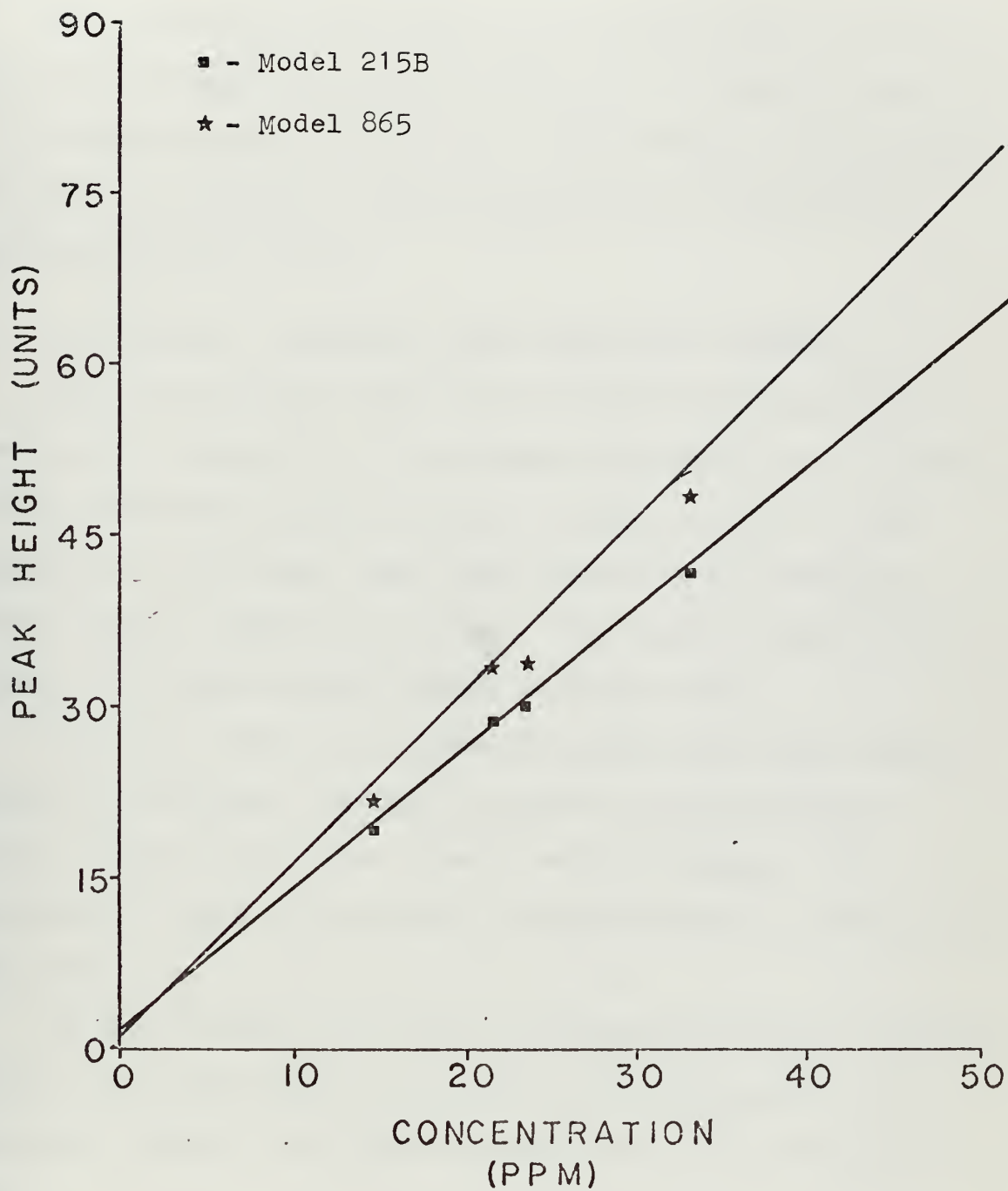


Figure 22. Oil in Bilge Water Peak Heights with the Oil Standard Curve vs. Concentration

A sample run of bilge water peak heights is shown in Fig 23. The high peaks are TC peaks and the low ones are IC channel peaks.

The mechanical adjustments encountered while operating the system changed the design from what is shown in Appendix B to what is shown in Figure 24. This design configuration represents the system construction for all experiments performed after 13 May.

F. ACID PURGE - INORGANIC TUBE COMPARISON RESULTS

The data from the acid purge comparison experiment is presented in Table VII. The reason why there is no IC peak height measurement after the acid purge, is that it was assumed, for all runs, that there would be no inorganic carbon after a sample was purged. The actual concentration values for comparison are found in Table VIII.

The bilge water test shows that the Acid Purge Method purged a few organic carbons, causing a high inorganic carbon reading and a low organic carbon reading. The difference in the concentration values of the two methods is low, however.

The test using the 50 ppm IC standard solution resulted in the Acid Purge Method not completely purging all the inorganic carbon. This was probably due to the technique used.

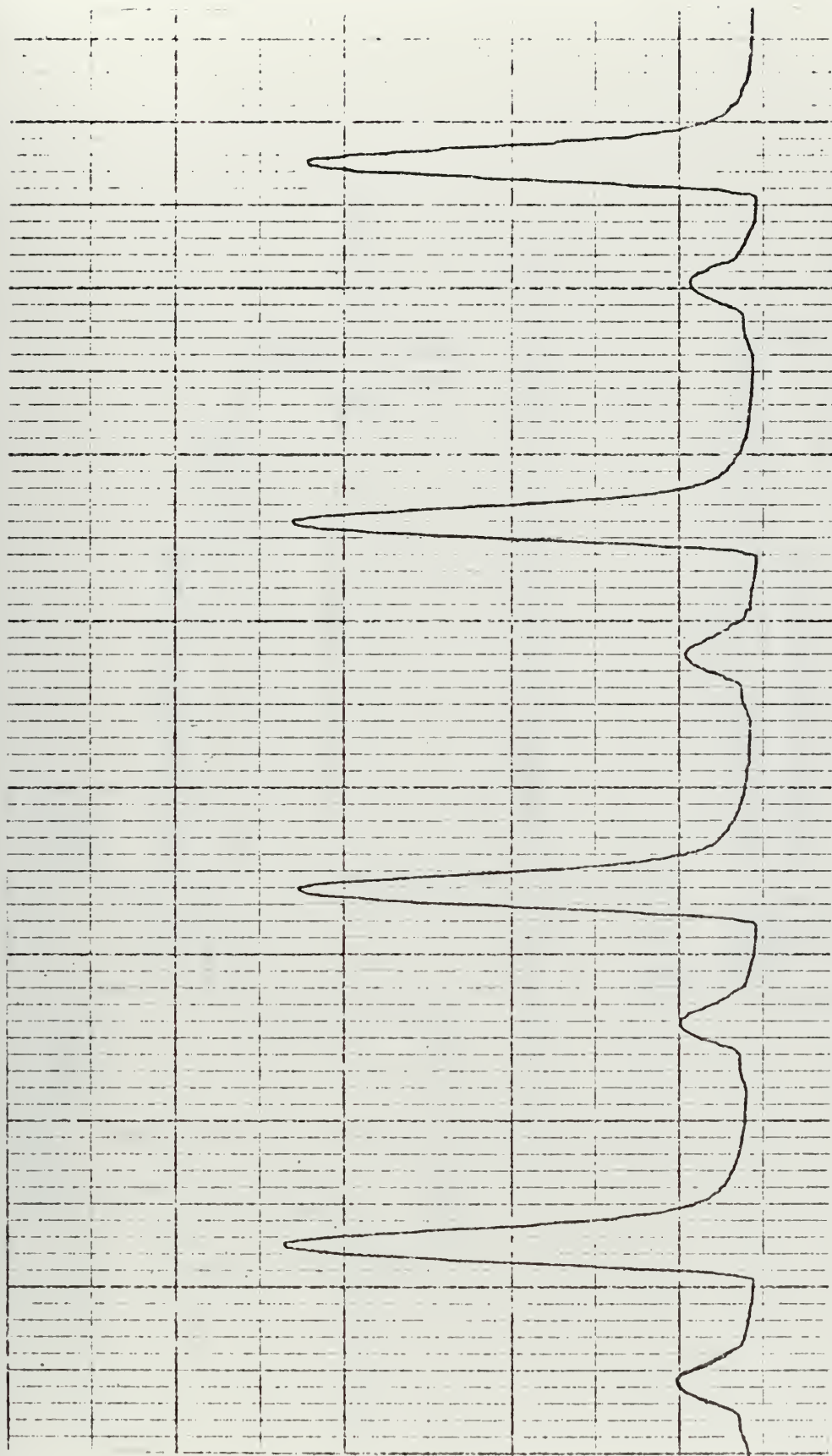


Figure 23. Sample Bilge Water Peak Heights

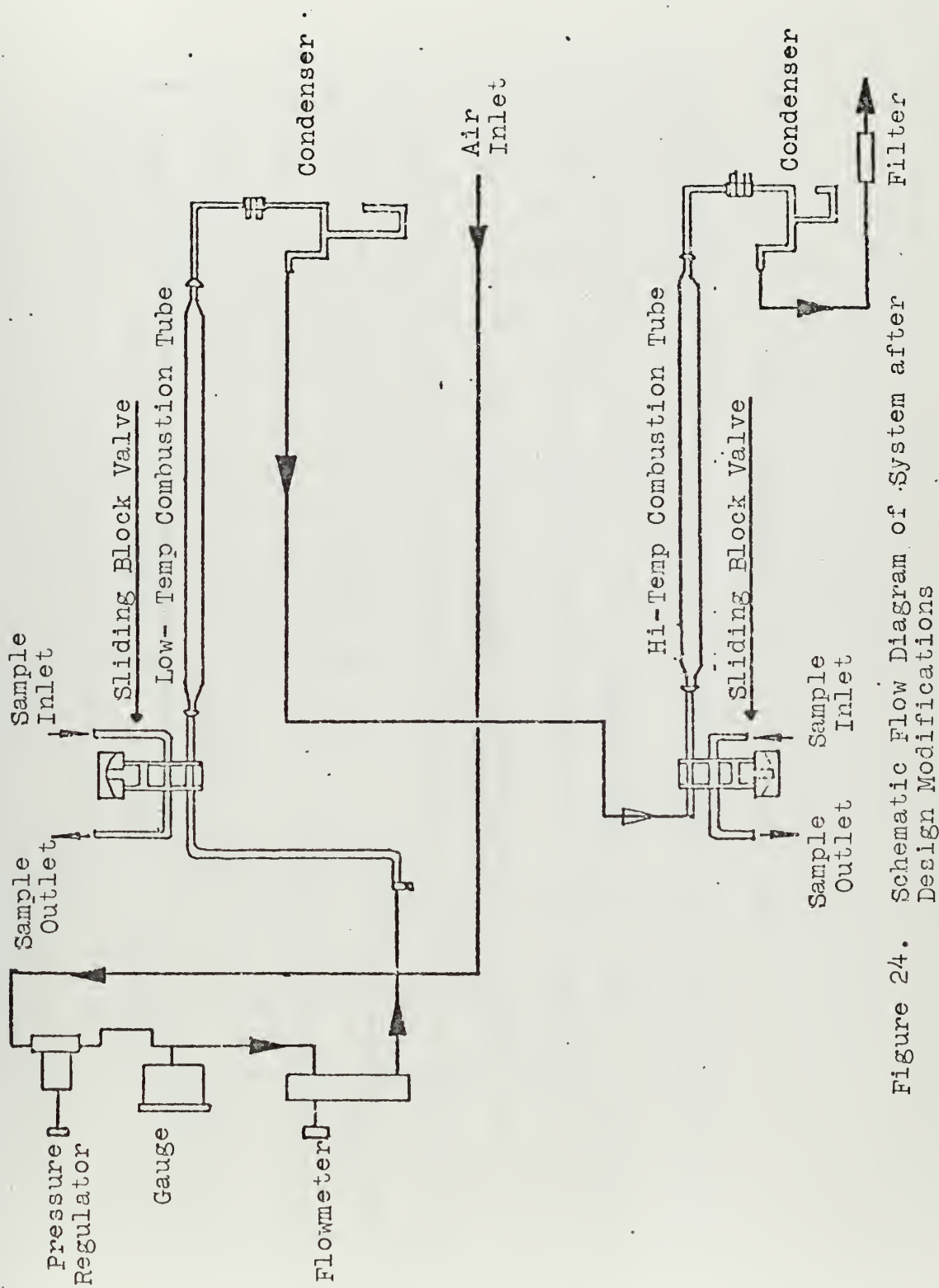


Figure 24. Schematic Flow Diagram of System after Design Modifications

DATE	ANALYZER	SAMPLE	TC PEAK	IC PEAK	ACID PURGE TC PEAK
13 May	215B	B.W. (NSRDC)	28.3 \pm 0.7	2.9 \pm 0.1	15.1 \pm 0.5
"	865	"	34.6 \pm 0.9	4.9 \pm 0.3	19.1 \pm 0.5
14 May	215B	"	25.9 \pm 0.7	2.4 \pm 0.2	13.4 \pm 0.6
"	865	"	31.5 \pm 0.7	4.5 \pm 0.4	17.1 \pm 0.9
"	215B	Tap Water	16.8 \pm 0.1	2.7 \pm 0.1	8.0 \pm 0.4
"	865	"	21.3 \pm 0.3	4.4 \pm 0.3	11.0 \pm 0.6
20 May	215B	50 ppm IC-STD	78.1 \pm 1.2	20.1 \pm 1.0	13.2 \pm 0.1
"	865	"	91.2 \pm 2.6	27.5 \pm 0.8	16.6 \pm 0.8

Table VII. Acid Purge Experiment Data

DATE	ANALYZER	SAMPLE	INORGANIC CONCENTRATION	IC-ACID PURGE CONCENTRATION
13 May	215B	B.W.	8.0 ppm	8.5 ppm
"	865	"	7.7 ppm	8.5 ppm
14 May	215B	"	7.0 ppm	8.3 ppm
"	865	"	7.0 ppm	8.8 ppm
"	215B	Tap Water	7.5 ppm	6.0 ppm
"	865	"	6.8 ppm	5.8 ppm
20 May	215B	50ppm IC	50.0 ppm	42.0 ppm
"	865	"	50.0 ppm	41.0 ppm

Table VIII. Acid Purge - Inorganic Channel Comparison

In the tap water tests, again, the Acid Purge Method did not completely purge all inorganic carbons. This is probably due to the fact that the complex inorganic carbon makeup of the tap water is not completely sparged by the Acid Purge test.

This experiment indicated a possible use of the Acid Purge technique for this application. A more detailed comparison, using bilge water, would have to be made before final remarks could be made in this regard.

V. CONCLUSIONS

A monitoring system was designed to automatically determine the concentration of oil in bilge water. Although testing is not complete, this monitor has partially proven its ability to achieve this purpose.

The calibration of the instrument showed that the Model 865 NDIR analyzer is a slightly better analyzer, as far as repeatability is concerned. Since the linearity control of the Model 865 is vastly superior to the Model 215B, future use of this system should be restricted to using the Model 865 NDIR analyzer.

The system was also found to need recalibration once a week during periods of heavy useage, i.e. eight hours per day. This recalibration could be accomplished by using the IC standard solution for both channels. Since the catalyst decay was found to be geometric, only one mid-range calibration point would be needed for recalibration. The new calibration curve would be less than the old one by the same factor, over its entire range.

The oil concentration experiment proved the ability of this system to accurately detect the concentration of any type of oil in water, with only one calibration curve. The particular oil standard curve that relates the recorder

peak height to the oil concentration was found to be 1.17 times the carbon standard calibration curve, as predicted by the theory. This system is unique among oil pollution monitors since it has the same response for all oil types.

The oil experiment showed that if the TOC content of all other sources in the sample, except for the oil, is known, then unknown oil concentration can be found. It also pointed out the problem of the grab sampling technique used by this system, in that a homogenous sample is needed to get a representative measurement. Fortunately, the bilge water that leaves present separator units is, for the most part, uniform.

The accuracy found in this experiment, 1.1 ppm, reflects the mixing method inaccuracies and not the measurement process. The standard deviations of the output reflects this idea in that the peak heights are accurate to about ± 0.5 ppm most of the time.

The preliminary study of bilge water shows that carbon input, from sources other than oil, is of low concentrations. This makes it possible to establish a standard organic and inorganic carbon content value for bilge water.

The tests of surface seawater indicate that it is only a minor contribution to the water content of a bilge. The carbon concentrations were much higher than those predicted in the theory and higher than the actual bilge water.

Seawater is, therefore, no more than one-third of the water make-up and is probably less.

The Acid Purge Method of organic carbon determination showed an ability for use in this application. The amount of phosphoric acid used and the time needed to purge a sample are factors that need to be investigated. The test performed in this research indicated a tendency for the Acid Purge Method to burn off some volatile organic carbon components of bilge water, when using the technique described in the Amendum to the TWRI Manual.

If a comparison of the two methods, Acid Purge and Direct Difference, were performed the factors that would need to be considered are the accuracy, the time per determination and the possible oil contamination of the system due to the acid causing the oil to plate out. The present research indicates that the Direct Difference Method, used by this system, was better in the test applications presented.

The prototype system, shown in Fig. 24, was the final product of this research. The instrument has shown that it can determine the oil concentration in water, independent of oil type. In order to make this determination, however, either the total carbon concentration of the bilge water must be known or the total organic carbon concentration of the bilge water must be known. It is in finding an operational standard for the latter of the two that future research should be aimed.

VI. RECOMMENDATIONS

The developed monitoring system fulfills most of the major specifications listed in the Introduction. Future work with this prototype should be directed towards decreasing the response time and installing the automatic controls listed in specifications (g) through (j).

The components of bilge water, listed in Ref. 1, should be tested and catalogued so that a standard can be found. More separated bilge water should be tested for the same reason.

A comparison of this instrument and an automatic Acid Purge Method system might be considered depending on whether or not users of that type of instrument feel it could perform in shipboard applications.

Although the sampling valve rulon can hold a 50 micron particle, this could be increased if the rulon thickness would be decreased enabling the sample hole diameter to be increased. The manufacturer of the rulon, Ionics, Inc., should be consulted in this matter.

A future mechanical refinement should be made with the condensers. They should be moved so that the inlet is directly underneath the combustion tube outlet. This would stop the condensation of the steam in the Tygon

connection tube. If the carrier air outlet of the condenser is pointed upward the water spill over to the filter would be reduced, thereby reducing the maintenance needed by the filter.

A program should be set up with NSRDC, Annapolis, to test bilge water samples and compare the results with those obtained by using the CCl_4 -I.R. Spectrometer Method.

APPENDIX A--BECKMAN MODEL 915

The Beckman Model 915 Total Organic Carbon Analyzer is used to directly determine the total carbon and inorganic carbon concentration of an aqueous solution through a rapid analysis of an aliquot of the solution. The total organic carbon is the difference between the two measurements.

The Model 915 consists of three interconnected units: a Sample-Inject/Furnace Module, a Model 215B or 865 Non-dispersive Infrared Analyzer and a Potentiometric Recorder.

The flow diagram of Fig.25 shows the two separate channels that are used. The low temperature flow path yields the inorganic carbon measurement and the high temperature path gives the total carbon measurement. Both channels operate in the same manner with the only differences being the combustion tube, the temperature and the catalyst.

Air, from an external cylinder, is directed into both channels. The air pressure and flow is controlled by the pressure regulator and the flowmeter. This controlled air flow proceeds through a check valve into the combustion tube. After coming out of the combustion tube, it passes through a condenser and goes into a sample select valve which either vents it to the atmosphere or directs it through a filter to the NDIR analyzer for analysis.

When an aqueous microsample is injected, by a syringe, the combustion tube converts the sample to CO_2 and steam. In the inorganic tube the temperature is low enough that only inorganic carbons convert to CO_2 . The high temperature tube oxidizes the entire sample. The CO_2 and steam is swept, by the air, through the condenser where the steam is condensed, leaving only the CO_2 . The CO_2 then passes through a filter and into the NDIR, which is sensitized to CO_2 . The electric signal output of the analyzer is registered as a peak on the recorder and this peak is directly proportional to the amount of carbon in the injected sample.

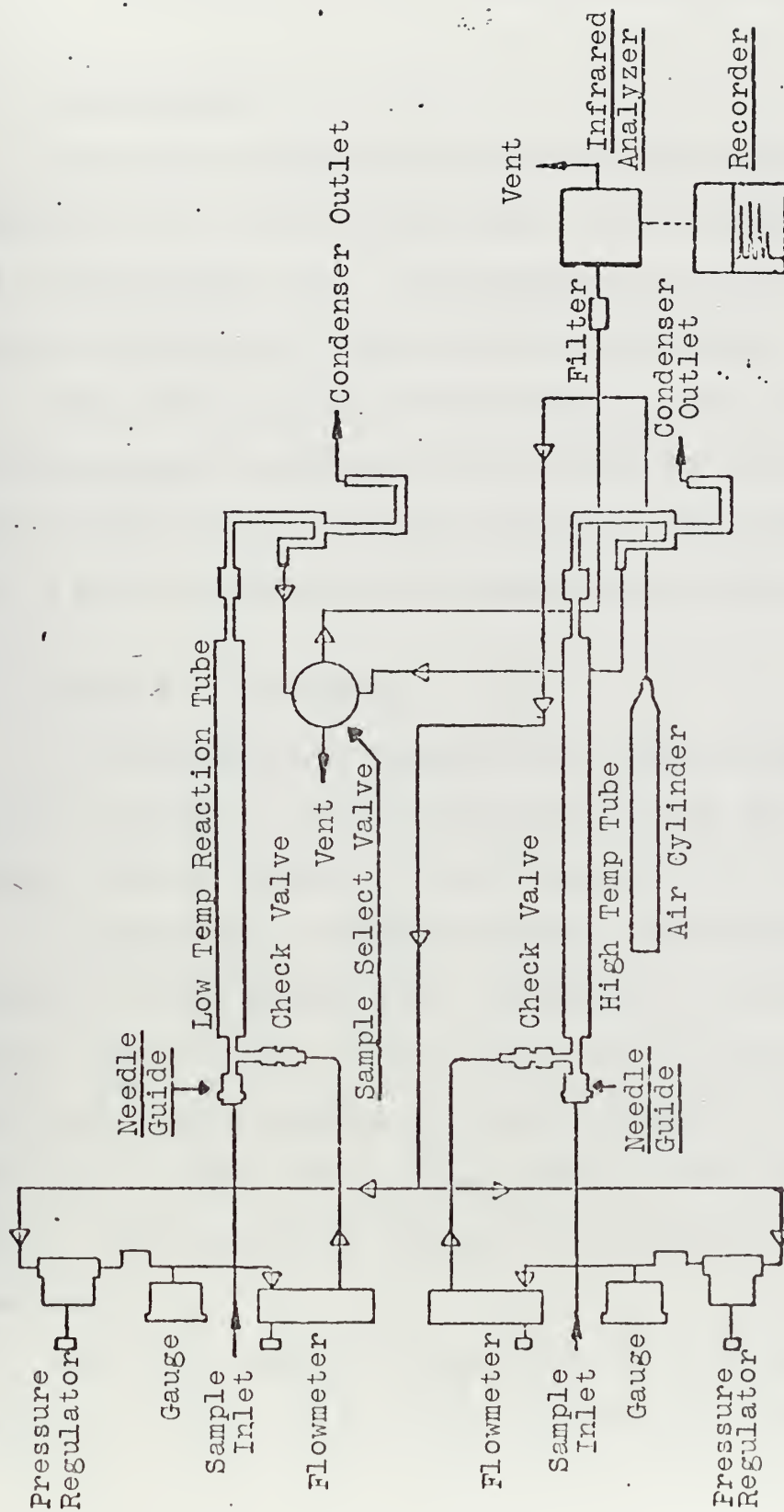


Figure 25. Schematic Flow Diagram of the Beckman 915

APPENDIX B-INITIAL DESIGN MODIFICATIONS

A. INTRODUCTION

The initial design modifications were made at the conclusion of a feasibility study, by this author, of the Beckman Model 915. The designs were drawn to meet the specifications listed in the Introduction.

The initial modification drawings and a description of the proposed operation are included to provide a continuity between the initial feasibility work done in Ref. 3 and the actual system described in this research.

B. CONCEPT OF OPERATION

In the continuous operation of this system, the air is flowing from a pressurized cylinder and the sample is flowing from an outlet on the discharge side of the separator.

Triggered by a timing sequence, the inorganic automatic injection block slides over, carrying a 20 ul sample, to the air inlet line. At the same time a valve blocks off the total carbon channel air flow and allows the air coming from the inorganic side to pass through the total carbon side. The time signal alerts the integrator to register negative.

The 20 ul sample is then shot, by 3 psi air, into the inorganic combustion tube which contains acid-soaked quartz

chips as a catalyst. The sample is oxidized and vaporized producing steam and CO_2 . The operating temperature is sufficiently low enough that only inorganic and some volatile organic carbons (VOC) are oxidized. The steam is then condensed and the CO_2 is swept through a Porapak Q column filter, which traps the VOC and allows the CO_2 to pass.

The CO_2 from the inorganics pass through the total carbon combustion tube (950°C) where any residual carbon in the air is oxidized. This maintains a constant baseline for both the total and inorganic carbon.

The CO_2 then passes through a MgSO_4 filter that filters out any seawater vapors. The CO_2 is swept into a Beckman Model 215B NDIR analyzer, or its equivalent, where the amount of CO_2 is measured and converted into a signal. The signal is then amplified and entered into the integrator which displays it on a digital read-out as a negative number.

Two and a half minutes after the first time signal, another time signal closes the inorganic inlet valve to the total carbon side. At the same time the auto-inject on the total carbon side is actuated and slides to the inject position. The time signal alerts the integrator to register positive.

The same time signal also closes the Porapak Q outlet valve, opens the air inlet to the filter and opens a vent

valve at the filter inlet. This flushes out the VOC. At 2.75 minutes from the original signal, the inorganic auto-inject is returned to its standby position and the air inlet on the filter outlet side is closed.

The 150 ul sample is then injected by the 3 psi air into the total carbon combustion tube. It is then oxidized and vaporized into CO₂ and steam, which is swept out. The steam is condensed and the CO₂ passes through the MgSO₄ filter into the NDIR analyzer, where the amount of CO₂ is measured. The resulting signal is amplified and entered into the integrator. The digital display will then show the total carbon measurement overcomes the negative value of the inorganic carbon measurement, the net result being the Total Organic Carbon (TOC). An alarm will be set for a +20 ppm reading.

At the end of five minutes from the first time signal, the total carbon auto-inject is reset to standby and the integrator is reset to zero. This procedure is repeated every half-hour.

The organic carbon contribution of the water will probably be set at a standard value and there will be a standard solution inlet for the periodic recalibration of the response curve. The integrator will be scaled to reflect the difference in the inorganic and total carbon sample sizes.

BECKMAN 915 WITH MODIFICATIONS

BRUCE D. TYLER

29 APRIL 1974

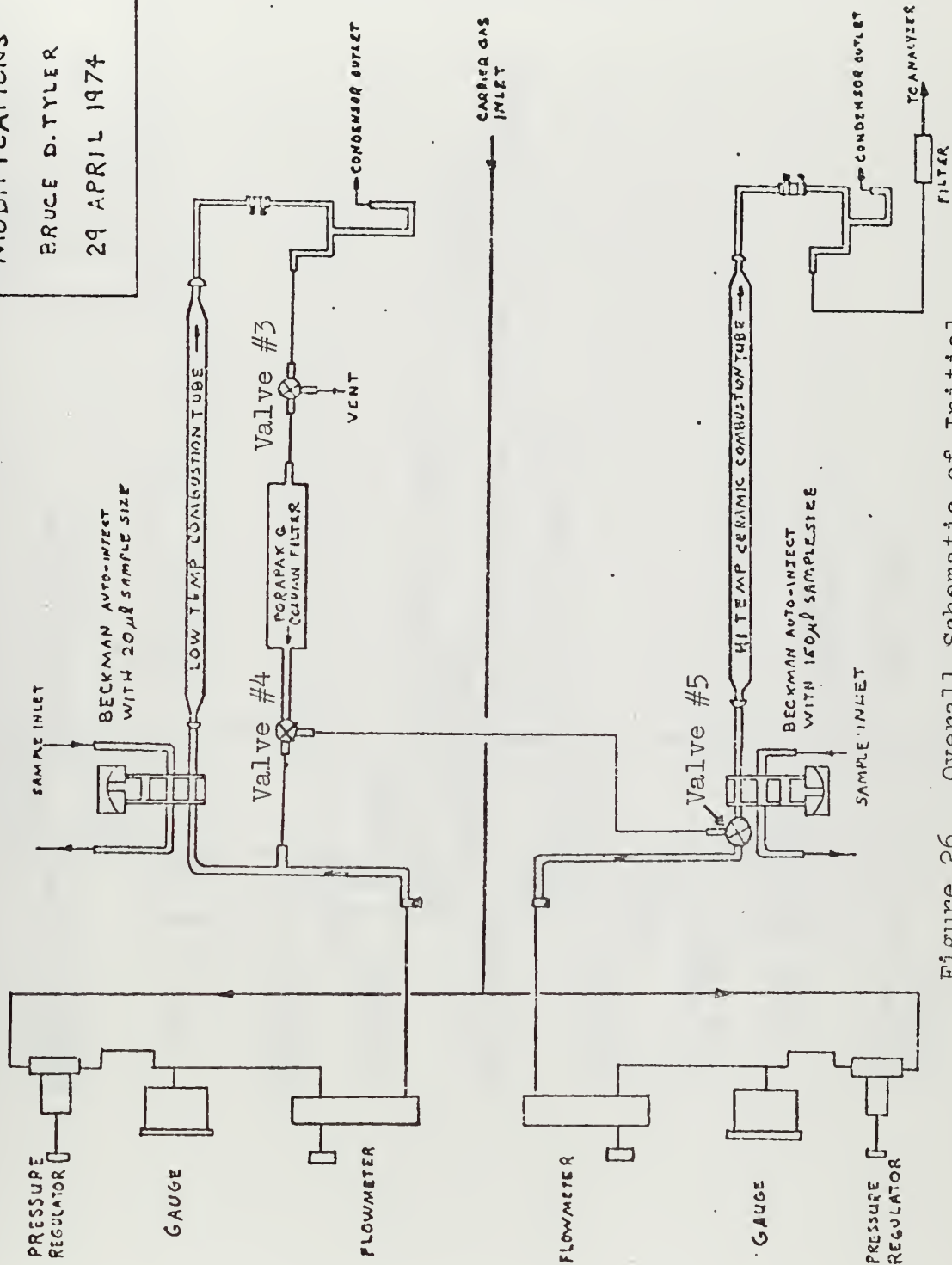


Figure 26. Overall Schematic of Initial Design Modifications

BECKMAN 915: AIR
SUPPLY CONTROL

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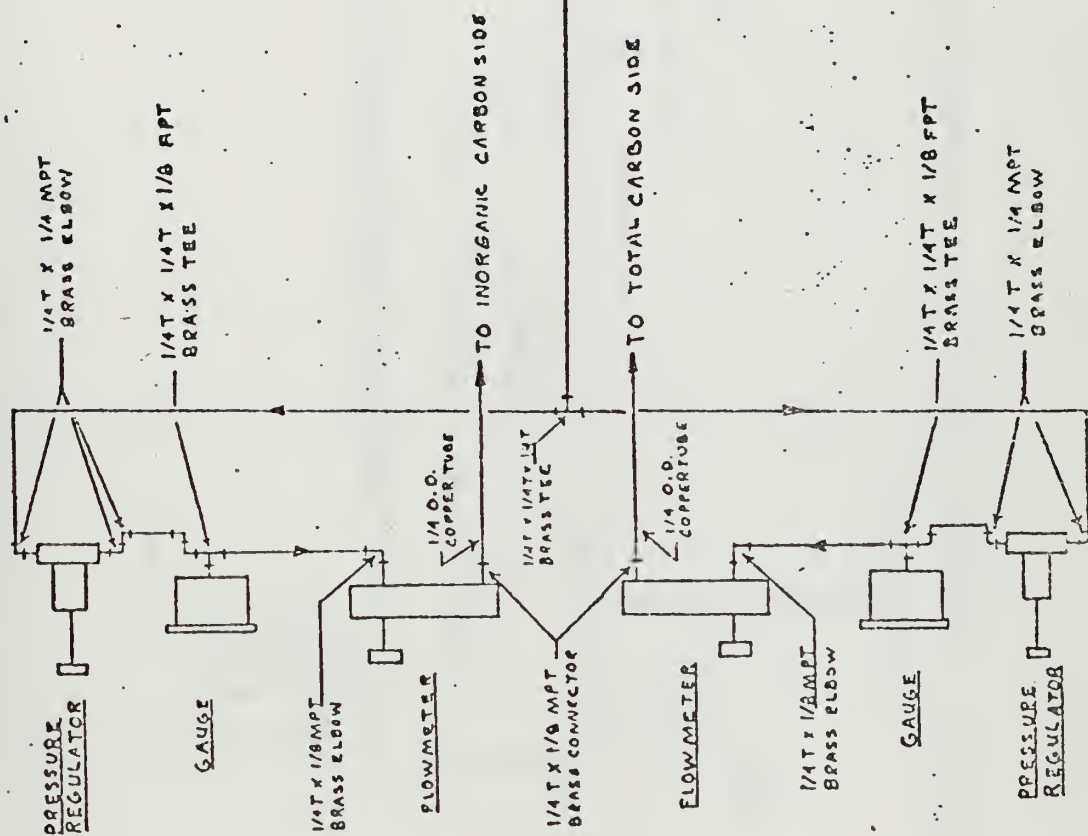


Figure 27. Detailed Schematic of Flow Control

INORGANIC CARBON

SIDE

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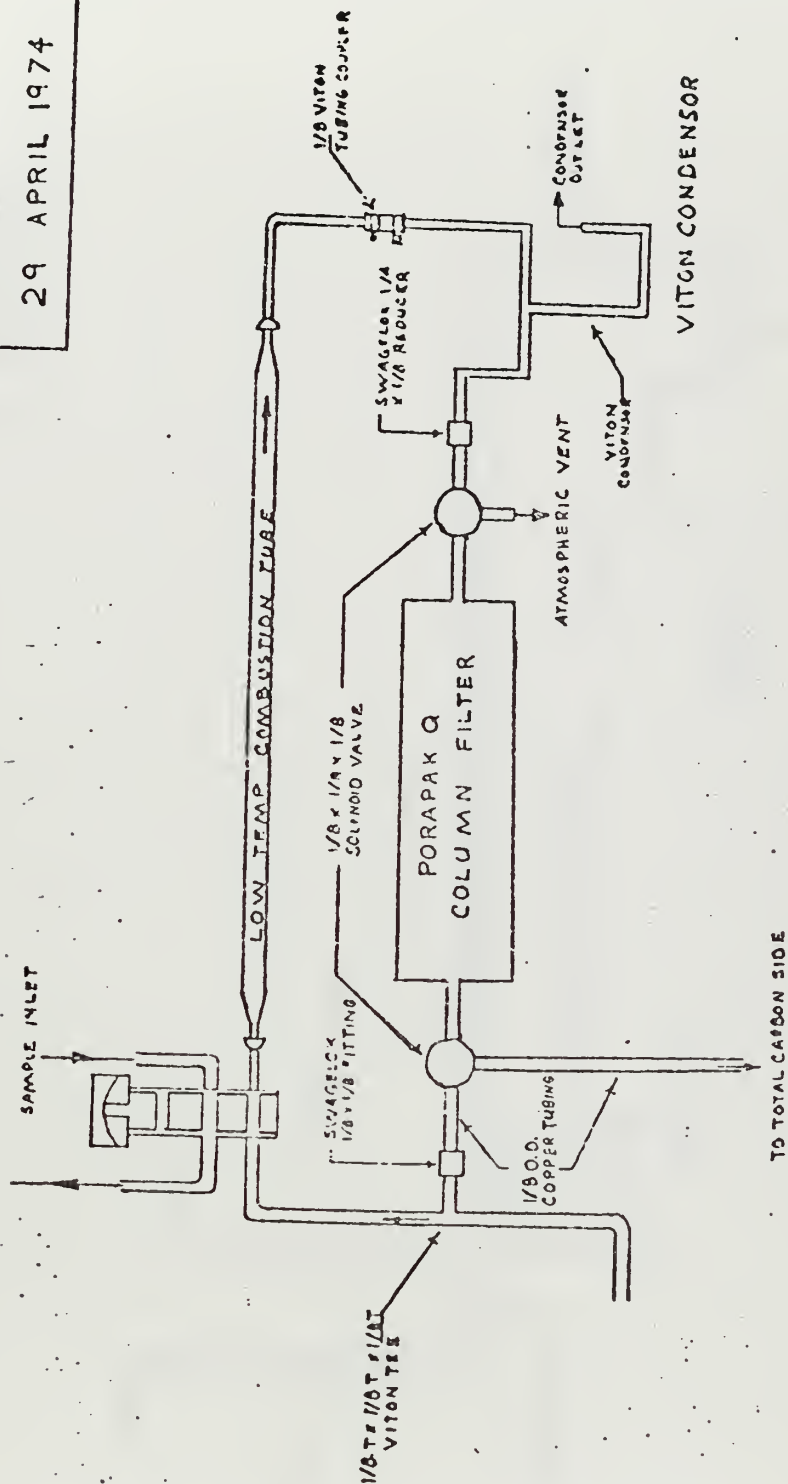


Figure 28. Detailed Schematic of Inorganic Carbon Channel

TOTAL CARBON
SIDE

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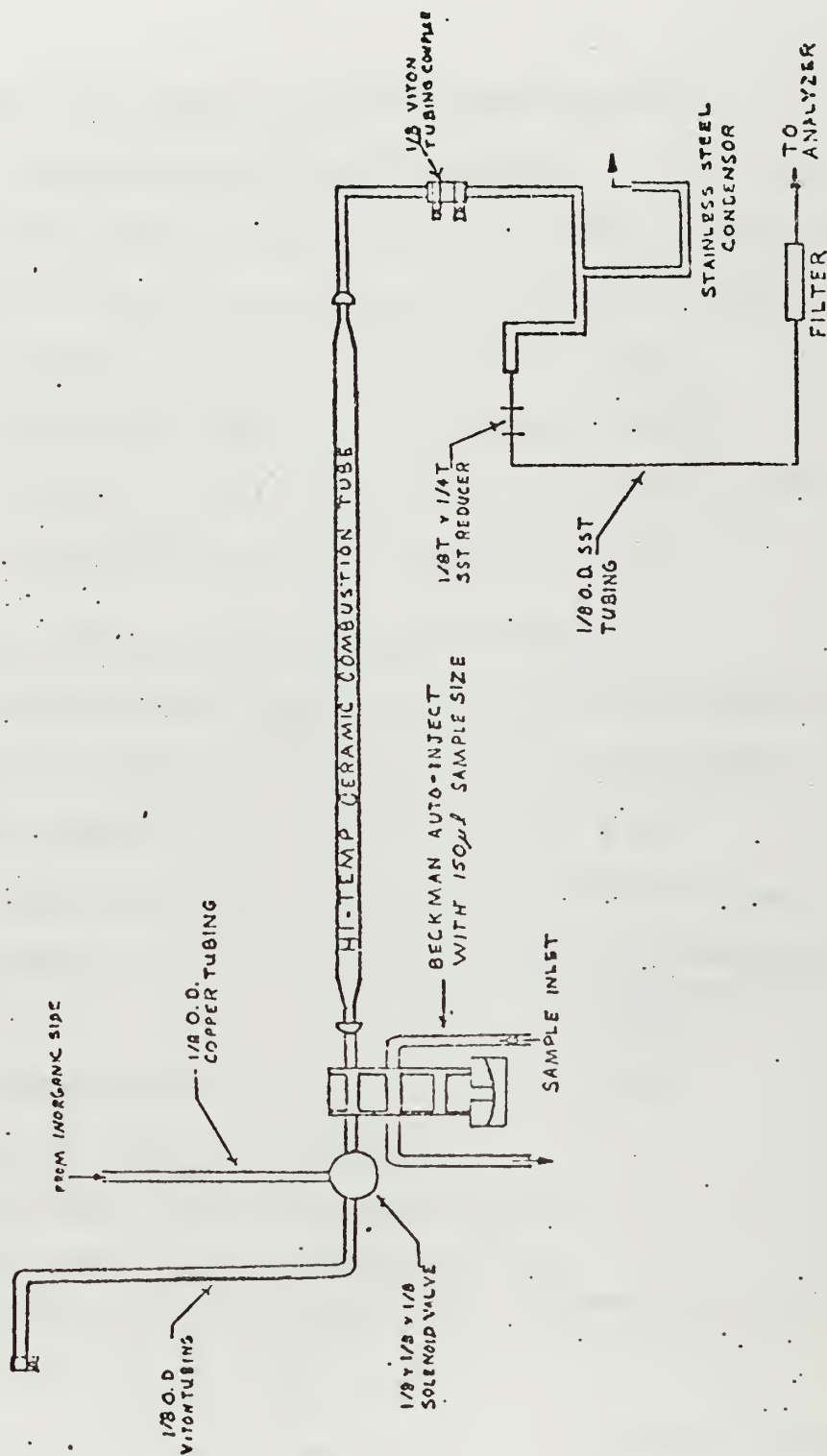


Figure 29. Detailed Schematic of Total Carbon Channel

APPENDIX C-EQUIPMENT OPERATING PARAMETERS

1. Beckman Model 915 Sample-Inject/Furnace Module

a. Total Carbon Channel Specifications

- (1) Carrier gas CO₂ - free Air
- (2) Flow rate 250 cc/min
- (3) Pressure 4 psi
- (4) Combustion tube Ceramic
- (5) Catalyst Cobalt oxide
- (6) Temperature 950°C

b. Inorganic Carbon Channel Specifications

- (1) Carrier gas CO₂ - free Air
- (2) Flow rate 250 cc/min
- (3) Pressure 4 psi
- (4) Combustion tube Vycor glass
- (5) Catalyst 85% Phosphoric
Acid-soaked Quartz
Chips
- (6) Temperature 150°C

2. Non-dispersive Infrared Analyzer

- a. Beckman Model 215B at a gain of 20.
- b. Beckman Model 865 at a gain of 700.

3. Hewlett-Packard Pontentiometric 10" Recorder set for .5in/min.

- a. Channel 1- 10 mv range
- b. Channel 2- 100 mv range

4. Ionics Sliding Block Valves at a 35 psi switching pressure.

- a. IC channel- 20 ul sample size
- b. TC channel- 40 ul sample size

APPENDIX D-OPERATION AND MAINTENANCE

A. OPERATION

Turn the high and low temperature ovens to ON and increase the flow rate to about 100 cc/min. Turn the NDIR to tune and observe the meter reading to make sure it is within the necessary limits. If not, adjust the tuning knob so the meter reading is within the limits. The oscillator tune increases with time. Then turn the NDIR to Range 1. Open the sliding block actuation air cylinder and adjust so the output is 35 psi. The CO₂- free air for the flow system should have about a 10 psi output from the cylinder. Let the system warm up until the oven operating temperatures are reached.

Adjust the pressure and flow control knobs so the carrier air is at 4 psi and 250 cc/min. Run distilled water through the injection circuit, using the first 20 ml as a rinse, by using the Masterflex pump on a setting of 5. Turn the voltage source on and adjust so the timer motor turns the cams at the revolution every four minutes, about 1.6 volts. Energize the solenoid panel. Let the distilled water run through the system until the peak heights are at the right level and the baseline is stabilized, about 20 minutes. The system is now ready for operation.

B. MAINTENANCE

The construction and operation of this system involves several maintenance procedures which are listed below:

1. Clean sample flow with distilled water.
2. Check the Hoke filter for signs of contamination every three weeks.
3. Check the NDIR tune every day.
4. Check the calibration points for catalyst breakdown and recalibrate about once a week.
5. Empty the condenser of its water every couple of days by loosening the Swagelok nut and letting the water leak out. Make sure the nut is retightened.
6. Turn the IC oven to OFF and the TC oven to LOW with a 3 psi air pressure and a 25 cc/min flow rate when not in use, except for extended periods of time in excess of two weeks.
7. Keep the NDIR analyzer running when not in use, except for extended periods of non-use.
8. Stabilize the instrument baseline using distilled water.
9. Clean the sample injection valves monthly.
10. Check for rulon deterioration weekly.
11. Check Swagelok fittings for rust.

12. The best indication of problems is the output peak height. If it is too low, the system may have a leak. Tailing peaks are a sign of system leaks or catalyst deterioration. Double peaks indicate problems in the flow system of the filter. Check for clogs and obstructions.
13. The catalyst should last several months before it needs to be replaced.

LIST OF REFERENCES

1. Smookler, A. L. and Hardin, J. W., Navy Shipboard Investigation of Oily Wastes, paper presented at 1975 Conference on Prevention and Control of Oil Pollution, San Francisco, California, 25-27 March 1975.
2. Prestia, J. V., Memorandum to Code 286, NSRDC, Annapolis, Subject: Summer of 1973 and following months; Report on, 11 July 1974.
3. Tyler, B. D., A System for the Measurement of the Concentration of Oil in Water, EN-496 Report, U. S. Naval Academy, Annapolis, Maryland, 15 May 1974.
4. Montgomery, H. A. C. and Thom, N. S., "Determination of Organic Carbon Concentrations in Water", Analyst, v. 87, p. 689, 1962.
5. Van Hall, C. E. and others, "Rapid Combustion Method For The Determination of Organic Substances in Aqueous Solutions," Analytical Chemistry, v. 35, no. 3, p. 315-319, March 1963.
6. Office of Naval Research Report 68-27T, Organic Carbon in the Gulf of Mexico, by Alan D. Fredricks and W. M. Sackett, p. 63, 1968.
7. Duursma, E. K. "Dissolved Organic Carbon, Nitrogen and Phosphorus in the Sea," Netherland Journal of Sea Research, v. 1, no. 1-2, p. 1-147, 1961.
8. Beckman Instruments, Inc., Total Organic Carbon Analyzer: Beckman Instructions 81706-A, October, 1968

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